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William Coffey, Yuri Kalmykov, Serguey Titov, William Dowling. Longest relaxation time of relaxation processes for classical and quantum Brownian motion in a potential: escape rate theory approach. Stuart A. Rice, Aaron R. Dinner. *Advances in Chemical Physics*, 153, Wiley, pp.111-309, 2013, *Advances in Chemical Physics*, 9781118477861. 10.1002/9781118571767.ch3 . hal-01898610

HAL Id: hal-01898610

<https://hal.science/hal-01898610>

Submitted on 24 May 2023

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LONGEST RELAXATION TIME OF RELAXATION PROCESSES FOR CLASSICAL AND QUANTUM BROWNIAN MOTION IN A POTENTIAL: ESCAPE RATE THEORY APPROACH

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I. INTRODUCTION

In this chapter, our objective is to review novel developments concerning the time behavior of relaxation (correlation) functions and their spectral properties as predicted by the nonlinear Langevin equations governing noise-activated escape from and relaxation in multistable potentials. One of the most important of these developments is that the Brownian dynamics of both a particle and a rigid body in a potential exhibit *universal* behavior that is common to a whole host of physical problems irrespective of the precise nature of the particular multistable system considered. This behavior is universal in the sense that in a multistable potential, the dynamic susceptibility spectra always exhibit a broad low-frequency relaxation loss peak due to *slow* noise-activated escape of the Brownian particles or rotators over the potential barriers, and so attributable to an activation process. Specific examples of this universal behavior include the relaxation processes appearing in the dielectric loss spectra of molecular liquids and solids, in the magnetic susceptibility spectra of magnetic nanoparticles, in the current–voltage characteristics of point Josephson junctions, and so on. In spite of the very extensive literature (see, e.g. [1–7]) concerning calculation of the longest relaxation (escape) time of both classical and quantum Brownian particles regarded as the inverse escape rate from a potential well, relatively few comparisons with the escape time yielded by the analytical and numerical solutions of the relevant classical or quantum master equations exist. The fundamental reason is the lack of an efficient algorithm for the solution of such master equations. Yet another difficulty has been the rather abstruse and hidden nature of the calculations surrounding the well-known Kramers turnover problem. This comprises the asymptotic calculation of the escape rate Γ in the underdamped regime where escape over a potential barrier is predominantly but not absolutely energy diffusion controlled and by extension the determination of an asymptotic formula for Γ irrespective of the dissipation to the bath. The best-known solution to the Kramers turnover problem is that given by Mel’nikov [8,9], Mel’nikov and Meshkov [10], and Larkin and Ovchinnikov (in the quantum case at relatively high temperatures where both thermal activation and quantum tunneling may coexist, which is the case of interest in this chapter) [11]. The quantum problem was solved by Larkin and Ovchinnikov in the underdamped regime in a semiclassical sense and extended in *ad hoc* fashion by Mel’nikov [8,9] to all values of the dissipation. This (seeming) defect was remedied later by the

rigorous solution given by Pollak et al. [12] (see also Ref. [4]) based on the mathematical description of friction as originating from linear coupling to a bath of harmonic oscillators. Since the calculations of Mel'nikov [8,9] and Larkin and Ovchinnikov [11] involving a depopulation factor (see below) are short on detail particularly in the quantum case and are rather difficult to follow, it is the primary purpose of this chapter to give (with the beginning graduate student in mind) a reasonably transparent résumé of these. Next, we show how the calculations may be adapted to a range of commonly encountered physical problems [13,14] involving the decay of metastable states. The results will then be compared with semianalytic solutions of the relevant classical or quantum master equation (for relatively high temperatures) based on the matrix continued fraction method.

The chapter is arranged as follows. Classical transition state theory (TST) for escape rate of a particle from a one-dimensional potential well and its generalization [4] to multidimensional systems is very briefly reviewed. The main results of including the effect of dissipative coupling to the bath as obtained by Kramers [15] using as model the phenomenological Langevin equation and its associated probability density diffusion equation in the phase space of a Brownian particle namely the Klein–Kramers equation [which is the Fokker–Planck equation (FPE) for particles or rigid rotators with separable and additive Hamiltonians] are then briefly given. The Langevin equation for a particle of mass m and momentum $p = m\dot{x}$, moving along the x -axis in a potential $V(x)$ is in terms of state variables (x, p)

$$\begin{aligned}\dot{x} &= p/m \\ \dot{p}(t) + \frac{\zeta}{m}p(t) + \frac{dV}{dx}[x(t)] &= F(t)\end{aligned}\tag{1}$$

where ζ is the viscous drag coefficient and $F(t)$ is the white noise driving force imposed by the bath that maintains the Brownian motion so that

$$\overline{F(t)} = 0, \quad \overline{F(t)F(t')} = 2k_{\text{B}}T\zeta\delta(t - t')\tag{2}$$

Here, k_{B} is the Boltzmann constant, T is the temperature, the overbar means the statistical average over an ensemble of particles that have all started at time t with the same initial position $x(t) = x$ and momentum $p(t) = p$. Equation (1) is interpreted here as a stochastic differential equation of the Stratonovich type [16,17]. The corresponding Klein–Kramers equation for the phase space evolution of the density $\rho(x, p, t)$ of the phase points (x, p) is

$$\frac{\partial \rho}{\partial t} = \frac{dV(x)}{dx} \frac{\partial \rho}{\partial p} - \frac{p}{m} \frac{\partial \rho}{\partial x} + \frac{\zeta}{m} \frac{\partial}{\partial p} \left(\rho p + mk_{\text{B}}T \frac{\partial \rho}{\partial p} \right)\tag{3}$$

This comprises the Liouville equation for a single particle augmented by a diffusion term accounting for the interaction of the particle with the heat bath.

The results of escape rate calculations [2] are the *spatially controlled diffusion* or intermediate to high damping (IHD) escape rate and the *energy-controlled diffusion* or very low damping (VLD) rate. Furthermore, it is emphasized that these are obtained using two *entirely distinct* approaches, namely, in IHD the escape rate is determined via the oscillator and inverted oscillator approximation for the potential at the well and at the saddle point and consequent linearization of the Langevin equation. In contrast for VLD, that is, energy-controlled diffusion, the *noisy* motion is simply regarded as a very small perturbation of the classical undamped librational motion in a well of a particle with energy equal to the barrier energy. Thus, the overall discussion now refers to particles on energy trajectories in an energy skin or boundary layer [16] very close to the barrier energy only such that the deviations from the Maxwell–Boltzmann distribution prevailing in the depths of the well are very significant. The classical Kramers turnover problem referring to the turnover of the escape rate from behavior proportional to the dissipation in VLD to the inverse behavior encountered in very high damping (VHD) is then formulated as a precursor to the calculation of the classical depopulation factor using the method proposed by Mel’nikov [8,9] and Meshkov and Mel’nikov [10]. Before explaining the details of their calculations, however, a description of Langer’s general theory [13] of the decay of metastable states that is *inter alia* the generalization of the IHD Kramers rate to a multidegree of freedom system is given. The importance of this result that holds when energy-controlled diffusion processes may be neglected is that it is equivalent [2] to a multidimensional TST rate in which the dissipative motion is modeled in the entire phase space of the system. Moreover, Langer’s escape rate formula may be obtained as a particular case (static friction) of multidimensional TST in the entire phase space of a metastable system coupled bilinearly to a bath of harmonic oscillators representing the effect of friction on the metastable system in question as treated by Pollak [18]. Returning now to the calculations of Mel’nikov [8,9] and Mel’nikov–Meshkov [10] that essentially rely on the original model of Kramers, the transformation for low damping, of the Klein–Kramers equation, into an energy–action diffusion equation is described in detail and its Green function is obtained. The Green function represents $g(E|E')$ the (Gaussian) transition probability that the energy of the lightly damped particle alters from E' to E in one cycle of the periodic motion infinitesimally close to the separatrix energy at the top of the well. It is in general sharply peaked since $E \approx E'$ meaning of course that the motion is deterministic so that the Green function becomes a delta function. The Gaussian kernel is then used (considering at first an isolated well) via the principle of superposition to construct an integral equation for the probability $f(E)$ per unit time of finding a particle with energy E in the barrier region near a classical turning point of the trajectory of the undamped librational motion of a particle in the well with energy equal to the barrier energy [2,8]. This equation may be solved by the Wiener–Hopf method ultimately yielding an expression for the underdamped escape rate in terms of a

depopulation factor expressing the phenomenon of the depletion (via thermal fluctuations [8]) of the population of the upper energy regions of the well occurring in the underdamped regime. It is then postulated in *ad hoc* fashion by Mel'nikov [8] (since the upper bound of both underdamped and IHD escapes is the TST rate) that the underdamped result may be extended to all values of the dissipation by simply multiplying it by the IHD escape rate. The trenchant criticisms (whereby the energy loss per cycle in the unstable normal mode of the combined particle and bath rather than that in the particle coordinate should be used) of this procedure embodied in Ref. [12] are then briefly reviewed and explained. In conclusion of the classical treatment (in accordance with the purposes of this chapter), the asymptotic escape rates calculated via the (asymptotic) turnover approach [8–10] for a representative number of disparate systems as detailed in the list of contents, are compared with those yielded by the corresponding classical Fokker–Planck equation.

In the quantum case (to paraphrase Mel'nikov [8]) in contrast to the escape rate for the classical regime where one starts from the Fokker–Planck equation we must instead specify the Hamiltonian of the entire system consisting of the particle and its heat bath recalling that one is interested in the escape rate for a system exhibiting viscous friction in the classical regime. In itself this condition is insufficient to define the entire system in a unique way. However, it is enough to determine the particle action that is obtained by integrating over the bath variables. This condition [8] is vital because then all models of the heat bath are equivalent as far as Γ is concerned provided they can reproduce the same Langevin equation in the classical limit.

Now Mel'nikov [8,9] proceeds in the manner of Kramers by using two different models of the bath. In the underdamped regime, he includes the interaction of a particle with a Boson bath by incorporating a term linear in the particle coordinate describing the effects of the (Johnson–Nyquist) noise (which is Gaussian) on the Hamiltonian (operator) of the particle. However, each quantum particle by its very nature now presents a range of possible quantum states as well as the thermal distribution of a huge assembly of such particles over a range of the possible states. The classical transition probability in energy space or Green function that forms the kernel of the integral equation for $f(E)$, therefore, must be replaced by the statistical density matrix (stemming from the evolution operator for the state vector) that includes both thermal and quantum effects. Hence, we can no longer calculate the Green function via the Fokker–Planck equation transformed to energy–action variables. Nevertheless, to determine the leading quantum corrections to the escape rate in the underdamped regime we may use the semiclassical approximation based on the JWKB (Green–Liouville) approximation [8,19] whereby the energy levels in the vicinity of the barrier are distributed quasicontinuously. Thus, the matrix elements of both the position \hat{x} and the evolution $\hat{\Phi}$ operators in the interaction representation may be represented in terms of the Fourier transform of the classical

trajectory. This is the essence of the method proposed by Larkin and Ovchinnikov. Their calculations ultimately yield an integral equation for the population of escaping quantum particles $f(E)$, where the kernel contains the quantum reflection factor for an inverted parabolic barrier as well as the Green function that is to be identified with the statistical density matrix calculated via the evolution operator $\hat{\Phi}$ in the appropriate semiclassical approximation. The function $f(E)$ now represents the quantum probability distribution of the escaping particles and is valid of course only at temperatures above the critical temperature [20] at which the parabolic approximation to the barrier fails. The integral equation for $f(E)$ differs from the classical one in two vital respects because (a) it includes the reflection factor for the inverted parabolic barrier and (b) the Green function must be calculated in a semiclassical manner. This was accomplished by Larkin and Ovchinnikov by essentially starting from the expression for the undamped classical trajectory of the librational motion in the well of a particle with energy equal to the barrier energy. The amplitude of a quantum transition from a state E' to E (recall that $E \approx E'$) in one cycle of the periodic motion under the influence of the noise may then be formally written down using the interaction picture in terms of the matrix elements of the time ordered system-bath operator $\hat{\Phi}(t)$ specifying the evolution of the state vector from state E' to E . Hence, the Green function may also be formally written down. Thus, by using the semiclassical approximation for the matrix elements of $\hat{\Phi}$ in the presence of the noise and averaging over the thermal distribution using the centered Gaussian properties of the Johnson–Nyquist quantum noise, we have a closed integral form for the Green function. This is rendered as the inverse Fourier transform of the characteristic function of the energy distribution. Now this Green function unlike the classical one always involves the quantum transition probability (Fermi’s Golden Rule) for the position operator in the presence of the noise in the first order of perturbation theory. Thus, unlike the classical case where the Green function is canonical in the sense that the sole (Kramers) parameter is the ratio of the action of the undamped periodic motion at the saddle energy to the thermal energy, the parameters of the quantum Green function depend on integrals involving the precise nature of the potential essentially because the semiclassical matrix elements are always involved.^{1,2}

¹ It should be noted that the integral equation for $f(E)$ is still of the Wiener–Hopf type and may be solved just as the classical case to yield the quantum escape rate in the semiclassical approximation in terms of a depopulation factor. However, the result is considerably more complicated than in the classical case because of the calculation of the matrix elements that is required for each particular potential.

² Having implicitly determined the population $f(E)$ of escaping particles, the escape rate or inverse of the lifetime of a quantum particle in the well may then be written down by integrating the energy distribution function multiplied by the quantum penetration or transmission factor for a parabolic barrier.

The most important practical consequence of the latter considerations is that in the classical case the depopulation factor, irrespective of the potential, is always essentially rendered in the same integral (or canonical) form. In contrast in the quantum case although a formal expression for the depopulation factor exists it must be calculated explicitly for each particular case using the semiclassical matrix elements giving rise to much more complicated calculations. These considerations of course refer to the underdamped regime. In the overdamped regime, Mel'nikov [8] assumed that the thermal bath is represented by a string (or transmission line) coupled to the particle and tightened in a direction perpendicular to the direction of motion of the particle. He then calculates the effective action of the particle as coupled to the string enabling him to determine the equilibrium distribution function and the density matrix using path integrals and thus, the IHD quantum rate at temperatures above the critical temperature where the inverted oscillator approximation to the barrier potential fails. However, the much simpler approach to the calculation of the IHD quantum rate due to Pollak [18] that is based on the recognition that the IHD rate is simply the TST rate in the entire phase space will be used here. Having determined both the quantum depopulation factor and the IHD rate, Mel'nikov [8] then used the same *ad hoc* assumption concerning the product of the IHD rate and the quantum depopulation factor to obtain a semiclassical expression for the escape rate that is valid for all values of the dissipation to the bath for a particle in an isolated well. Simultaneously he gave a variety of results for particles in periodic potentials and so on. As mentioned above, we shall attempt to give the details and an appraisal of the various high-temperature quantum calculations. Moreover, just as we have accomplished in the classical case we shall compare the results yielded by the depopulation factor method with the perturbation solution obtained from quantum master equations based on Wigner's phase space representation of quantum mechanics in the appropriate order of perturbation theory in Planck's constant and the inverse temperature.

II. ESCAPE RATE FOR CLASSICAL BROWNIAN MOTION

A. Review of the Kramers' Results: Escape Rate from a Single Isolated Well

1. Kramers' Escape Rate Theory

The origin of modern reaction rate theory stems from the 1880s when Arrhenius [1–5] proposed, from an analysis of the experimental data, that the rate coefficient in a chemical reaction should obey the law

$$\Gamma = \nu_0 e^{-\Delta V} \quad (4)$$

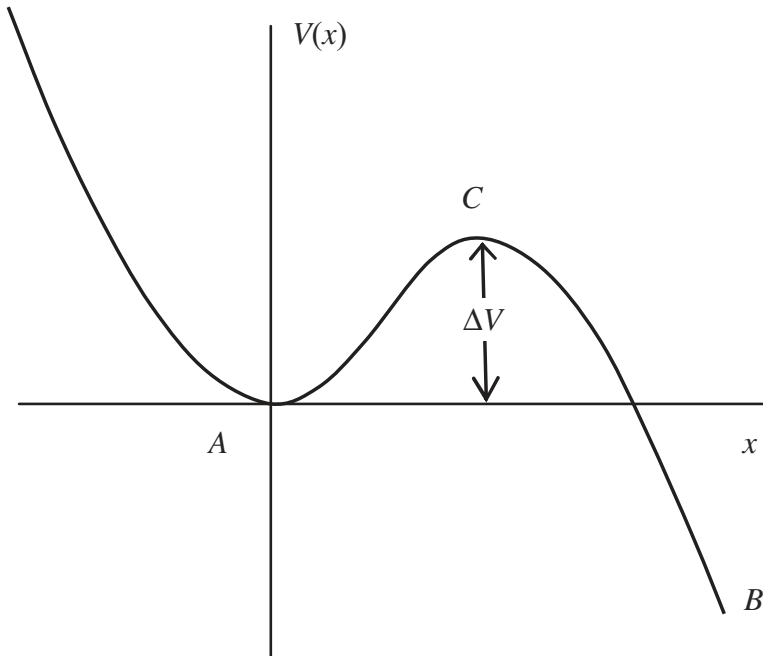


Figure 1. Single-well potential function as the simplest example of escape over a barrier. Particles are initially trapped in the well near the point A by a high-potential barrier at the point C . They are thermalized very rapidly in the well. Due to thermal agitation, however, very few may attain enough energy to escape over the barrier into region B , from which they never return (a sink of probability). The barrier C is assumed large to ensure that the rate of escape of particles is very small.

where ΔV denotes the dimensionless (i.e., in units of $k_B T$) threshold energy for activation and v_0 is a prefactor [3]. After very many developments summarized in Ref. [2], this equation led to the concept of chemical reactions, as an assembly of particles situated at the bottom of a potential well and subjected to thermal agitation. Rare members of this assembly attain enough energy to escape over the potential hill due to the shuttling action of the thermal agitation and never return [2] (see Fig. 1), so constituting a model of a chemical reaction.

The escape over the potential barrier represents the breaking of a chemical bond [2]. The Arrhenius law for the escape rate Γ (reaction velocity in the case of chemical reactions) of particles that are initially trapped in a potential well at A , and that may subsequently, under the influence of thermal agitation, escape over a high barrier of height ΔV at C and never return to A , may be written using TST [2,4] as

$$\Gamma^{\text{TST}} = \frac{\omega_A}{2\pi} e^{-\Delta V} \quad (5)$$

Here, the attempt frequency, ω_A , is the angular frequency of a particle executing small oscillations about the bottom of a well. The barrier arises from the potential function of some external force, which may be electrical, magnetic, gravitational, and so on. The formula represents an attempt frequency times a Boltzmann factor, which weighs the escape from the well. We emphasize [4] that Γ^{TST} does not depend on the coupling between the molecules and their environment and *depends only on the parameters that characterize the equilibrium distribution*. A simple and transparent derivation of Eq. (5) in terms of the forward flux at the transition state $x = x_C$ is given by Nitzan [4] who remarks that Eq. (5) yields the correct TST rate provided that $V(x)$ is taken as the *effective* potential of the reaction coordinate.

In other words, $V(x)$ is the potential of mean force along this coordinate when all other degrees of freedom are in thermal equilibrium at any given point on it.

Now the generalization of Eq. (5) to an $(N+1)$ -dimensional system with a separable and additive Hamiltonian has also been described by Nitzan [4] and is

$$\Gamma^{\text{TST}} = \frac{1}{2\pi} \left(\prod_{i=0}^N \omega_{A,i} / \prod_{i=1}^N \omega_{C,i} \right) e^{-\Delta V} \quad (6)$$

Here, $\omega_{A,i}$ are the angular frequencies of the modes that diagonalize the Hessian of the potential in the vicinity of the well bottom x_A^{N+1} , where x^{N+1} designates the collection of coordinates (x_0, x_1, \dots, x_N) while $\omega_{C,i}$ are the angular frequencies of the modes that diagonalize the Hessian at the saddle point x_C^{N+1} . We emphasize that the product of frequencies in the denominator of Eq. (6) is over the *stable* modes associated with the saddle point C . Thus, the imaginary frequency ω_C associated with the *unstable* barrier-crossing mode along the reaction coordinate is excluded so that the TST rate is given [2] in terms of the product of all *stable* mode frequencies at the minimum and the inverse product of *stable* mode frequencies at the saddle point. Now [4] if the unstable mode associated with this coordinate can also be identified in the vicinity of the well bottom and has frequency $\omega_{A,0}$ say then we may write [4]

$$\Gamma^{\text{TST}} = \frac{\omega_{A,0}}{2\pi} e^{-F_C/(k_B T)} \quad (7)$$

where the activation free energy ($dx^N = dx_1, \dots, dx_N$)

$$F_C = -k_B T \ln \int dx^N e^{-V(x^{N+1})} = W(x_{C,0}) = T (k_B \Delta V - S_C) \quad (8)$$

and

$$S_C = k_B \ln \left(\prod_{i=1}^N \frac{\omega_{A,i}}{\omega_{C,i}} \right) \quad (9)$$

where S_C is the entropic component of the activation free energy. These conclusions which emphasize that we are dealing with a free energy surface associated with a free energy barrier directly follow from writing Eq. (6) in the effective one-dimensional form of Eq. (7). Equations (6)–(9) are of the utmost importance in the generalization of the intermediate to high damping Kramers escape rate to many dimensions due to Langer [13] (see Section II.A.4). Here, the problem is equivalent to a multidimensional TST where the dissipative motion is modeled in the complete phase space of the system whereby one treats explicitly the coupling

to the bath degrees of freedom as accomplished by Pollak [18]. For this purpose Eq. (6) is commonly rewritten (details in Ref. [2]) in the form

$$\Gamma^{\text{TST}} = \frac{k_{\text{B}}T}{2\pi\hbar} \frac{Z^{\#}}{Z_0} e^{-\Delta V} \quad (10)$$

where

$$Z_0 = \prod_{i=0}^N \frac{k_{\text{B}}T}{\hbar\omega_{\text{A},i}}, \quad Z^{\#} = \prod_{i=1}^N \frac{k_{\text{B}}T}{\hbar\omega_{\text{C},i}} \quad (11)$$

are the harmonic approximations to the well and saddle partition functions, respectively. Thus, the (harmonic) TST rate is simply the ratio of partition functions at the transition state and reactants [21].³

Since a large part of this chapter will be concerned with quantum effects in reaction rate theory, it is appropriate at this juncture to refer to the quantum generalization of Eq. (5) (details in Ref. [20]). We have

$$\Gamma \approx \frac{\omega_{\text{A}}}{2\pi} \Xi e^{-\Delta V} \quad (12)$$

where

$$\Xi = \frac{\omega_{\text{C}}}{\omega_{\text{A}}} \frac{\sinh[\hbar\omega_{\text{A}}/(2k_{\text{B}}T)]}{\sin[\hbar\omega_{\text{C}}/(2k_{\text{B}}T)]} = 1 + \frac{1}{24} \left[\left(\frac{\hbar\omega_{\text{C}}}{k_{\text{B}}T} \right)^2 + \left(\frac{\hbar\omega_{\text{A}}}{k_{\text{B}}T} \right)^2 \right] + \dots \quad (13)$$

is the quantum correction to the classical TST result. It should be noted that the quantum correction factor Ξ represents an effective lowering of the potential barrier so enhancing the escape rate [20]. An important feature of Eq. (12) is that the prefactor diverges at a crossover temperature T_{C} given by $T_{\text{C}} = \hbar\omega_{\text{C}}/(2\pi k_{\text{B}})$. The divergence occurs because the parabolic (or inverted oscillator) approximation for the potential is only valid near the top of the barrier. However, at very low temperatures $T \ll T_{\text{C}}$, where the particle is near the bottom of the well, the parabolic approximation to the barrier shape is not sufficient (see [22, Chapter 12]). On the other hand, for $T > T_{\text{C}}$ transitions near the top of the barrier dominate, so that the parabolic approximation is accurate [20]. Equation (13) was derived [20] using the Wigner function method. The simplest way of deriving it is, however, to recall [22] that the escape rate may be written as

$$\Gamma = Z_{\text{A}}^{-1} \int_{-\infty}^{\infty} w(E) e^{-E/(k_{\text{B}}T)} dE \quad (14)$$

³ The foregoing approach is generally referred to as harmonic transition state theory.

where

$$w(E) = \left[1 + e^{2\pi(V_C - E)/\hbar\omega_C} \right]^{-1} \quad (15)$$

which is the exact quantum transmission (penetration) coefficient (ignoring dissipation) of a parabolic barrier [23]. Hence,

$$\Gamma = \frac{\hbar\omega_C}{2Z_A \sin [\hbar\omega_C/(2k_B T)]} e^{-V_C/(k_B T)} \quad (16)$$

Furthermore, near the bottom of the well the partition function Z_A is approximated by that of a harmonic oscillator so that

$$Z_A \sim \frac{\pi\hbar}{\sinh [\hbar\omega_A/(2k_B T)]} e^{-V_A/(k_B T)} \quad (17)$$

Hence, we have Eq. (12). The quantum correction to the exponential factor in Eq. (12) was essentially obtained by Wigner [24]. The multidimensional generalization of (12) where at the transition state we have N real oscillators with frequencies $\omega_{C,j}, j = 1, \dots, N$ and one imaginary frequency oscillator with frequency $\omega_{C,0}$ is [2]

$$\Gamma = \frac{\omega_{C,0}}{2\pi} \frac{\sinh [\hbar\omega_{A,0}/(2k_B T)]}{\sin [\hbar\omega_{C,0}/(2k_B T)]} \left(\prod_{j=1}^N \frac{\sinh [\hbar\omega_{A,j}/(2k_B T)]}{\sinh [\hbar\omega_{C,j}/(2k_B T)]} \right) e^{-\Delta V} \quad (18)$$

Returning to the classical case it seems that a very unsatisfactory feature of TST is that it predicts *escape in the absence of coupling to a heat bath* in contradiction to the fluctuation–dissipation theorem. This is so because TST relies entirely [4] on the concept of *equilibrium flux* calculated, for example, on the basis of the Maxwellian velocity distribution through a carefully chosen surface that often provides a good approximation to the observed nonequilibrium rate. Moreover, for high-energy barriers, this procedure is often so successful that dynamical effects lead to relatively small corrections. Nevertheless, this defect was remedied and reaction rate theory was firmly set in the framework of nonequilibrium statistical mechanics by the pioneering work of Kramers [15]. He chose [in order to take into account *nonequilibrium effects* in the barrier-crossing process that manifest themselves as a frictional dependence (i.e., a coupling to the heat bath of the prefactor in the TST formula)] as a microscopic model of a chemical reaction, a classical particle moving in a one-dimensional potential (see Fig. 1). The fact that a typical particle is embedded in a heat bath is modeled by the Brownian motion. This represents (essentially through a dissipation parameter) in the single-particle distribution function, all the remaining degrees of freedom of the system consisting of the selected particle and the heat bath, which is in *perpetual thermal*

equilibrium at temperature T . In the Kramers model [1,2,15], the particle coordinate x represents the *reaction coordinate* (i.e., the distance between two fragments of a dissociated molecule—a concept first introduced by Christiansen [1,2] in 1936). The value of this coordinate, x_A , at the first minimum of the potential represents the *reaction state*, the value, x_B , significantly over the summit of the well at B (i.e., when the particle has crossed over the summit) represents the *product state*, and the value, x_C , at the saddle point, represents the *transition state*. We remark that in his calculations of 1940, Kramers [3,15] assumed that the particles are initially trapped in a well near the minimum of the potential at the point A . They then receive energy from the surroundings so that a Maxwell–Boltzmann distribution is rapidly attained in the well. Over a long period of time, however, rare particles gain energy in excess of the barrier height ΔV . Kramers then assumed that these particles escape over the barrier C (so that there is a perturbation of the Maxwell–Boltzmann distribution in the well) and reach a minimum at B , which is of lower energy than A , and once there, never return. We list the assumptions of Kramers:

- (1) The particles are initially trapped in A (which is a *source* of probability).
- (2) The barrier heights are very large compared with $k_B T$ (Kramers takes k_B to be 1).
- (3) In the well, the number of particles with energy between E and $E + dE$ is proportional to $\exp[-E/(k_B T)] dE$, that is, a Maxwell–Boltzmann distribution is attained extremely rapidly in the well.
- (4) Quantum effects are negligible.
- (5) The escape of particles over the barrier is very slow (i.e., is a quasistationary process) so that the disturbance to the Maxwell–Boltzmann distribution (postulate 3) is almost negligible at all times.
- (6) Once a particle escapes over the barrier it practically never returns (i.e., B is a *sink* of probability).
- (7) A typical particle of the reacting system may be modeled by the theory of the Brownian motion, including the inertia of the particles.

It is worth mentioning here that assumption 5 above relies heavily on assumption 2. If the barrier is too low, the particles escape too quickly to allow a Boltzmann distribution to be set up in the well. On the other hand, if the barrier ΔV is high, before many particles can escape, the Boltzmann distribution is set up. As required by postulate 3, we assume, therefore, that ΔV is at least of the order, say, 5.

The model, which yields explicit formulas for the escape rate for very low and intermediate to high dissipative coupling to the bath (so including nonequilibrium effects in the TST formula), is ubiquitous in any physical system in which noise-activated escape from a potential well exists. It has recently attained new importance in connection with fields as diverse as dielectric relaxation of nematic

liquid crystals [25], magnetic relaxation of fine ferromagnetic particles [26], laser physics [27,28], and Josephson junctions [16].

Kramers' objective was to calculate the (dynamical) prefactor μ in the escape rate, namely,

$$\Gamma = \mu \Gamma^{\text{TST}} = \mu \frac{\omega_A}{2\pi} e^{-\Delta V} \quad (19)$$

from a *microscopic model* of the chemical reaction. Now a microscopic model of the reacting system incorporating dissipation (namely, an assembly of Brownian particles in a potential well) is used to determine the nonequilibrium part μ of the prefactor. Thus, μ indicates that the prefactor is closely associated both with the *stochastic differential equation* underlying the Brownian motion, that is, the Langevin equation for the evolution of the random variables (position and momentum constituting the state vector) and the *associated probability density diffusion equation* describing the evolution of the density of the realizations (phase points) of these random variables in phase space. This as we show is the FPE, which like the Boltzmann equation, is a *closed* equation for the *single-particle* probability density function (PDF).

Now by considering the quasistationary solution of the Klein–Kramers (FPE) equation, Kramers discovered two asymptotic formulas for the escape rate out of a well for the single degree of freedom system governed by the Langevin equation for a particle moving along the x -axis under the influence of a potential $V(x)$. The first is the IHD formula (or spatially controlled diffusion rate)

$$\Gamma^{\text{IHD}} = \left\{ \left[1 + \beta^2 / (4\omega_C^2) \right]^{1/2} - \beta / (2\omega_C) \right\} \Gamma^{\text{TST}} \quad (20)$$

where ω_C is the characteristic frequency of the inverted oscillator approximation to the potential $V(x)$ in the vicinity of the barrier and $\beta = \frac{s}{m}$. In the IHD formula, the correction μ to the TST results in the prefactor of Eq. (19) is essentially the positive eigenvalue (characterizing the unstable barrier-crossing mode) of the Langevin equation associated with the Klein–Kramers equation (however omitting the noise) linearized about the saddle point of the potential $V(x)$. In the case considered by Kramers, this is a one-dimensional maximum. A further discussion of this is given later.

Equation (20) formally holds [3], when the energy loss per cycle of the motion of a particle librating in the well with energy equal to the barrier energy E_C , is significantly greater than $k_B T$.

The energy loss per cycle of the motion of a barrier-crossing particle is $\beta S(E_C)$, where E_C is the energy contour through the saddle point of the potential and S is the action evaluated at the barrier energy $E = E_C$. This criterion effectively follows from the Kramers very low damping result (see below). The IHD asymptotic formula is derived by supposing

- (i) that the barrier is so high and the dissipative coupling to the bath so strong that a Maxwell–Boltzmann distribution always holds at the bottom of the well and
- (ii) that the Langevin equation may be linearized in the region very close to the summit of the potential well, meaning that all the coefficients in the corresponding Klein–Kramers equation are linear in the positions and velocities.

If these simplifications can be made, then the Klein–Kramers equation, although it still remains an equation in the two phase variables (x, p) , may be integrated by introducing an independent variable that is a linear combination of x and p so that it becomes an ordinary differential equation in a single variable.

A particular case of the IHD formula is VHD, where Γ from Eq. (20) becomes

$$\Gamma^{\text{VHD}} = \frac{\omega_C}{\beta} \Gamma^{\text{TST}} = \frac{\omega_A \omega_C}{2\pi\beta} e^{-\Delta V} \quad (21)$$

Here, the quasistationary solution may be obtained directly in integral form by quadratures by using the Smoluchowski equation [3,4] for the evolution of the configuration space density and the high-barrier limit of the solution (which is appropriate to the escape rate) may be found by the method of steepest descents.

For small friction β (such that $\beta S(E_C) \ll k_B T$), however, the IHD formula fails predicting just as the TST formula, escape in the *absence of coupling to the bath* because [3] the tacit assumption that the particles approaching the barrier from the depths of the well are in thermal equilibrium (so that the stationary solution applies) is violated (due to the smallness of the dissipation of energy to the bath). Thus, the spatial region of significant departure from the Maxwell–Boltzmann distribution in the well extends far beyond the region, where the potential may be sensibly approximated by an inverted parabola.

Kramers showed how his second formula valid in the VLD case, where the energy loss per cycle $\beta S(E_C)$ of a librating particle is very much less than $k_B T$, may be obtained by again reducing the Klein–Kramers equation to a partial differential equation in a single spatial variable. This variable is the *energy* or, equivalently, the *action*. Here, the noisy energy trajectories associated with an escaping particle are almost closed, that is, almost periodic so that they differ but little from those of the undamped librational motion in a well with energy corresponding to the saddle energy ΔV or E_C . Kramers then solved the VLD problem by writing the Klein–Kramers equation in angle–action (or angle–energy) variables (the angle is the *phase* or *instantaneous state* of the system along an energy trajectory) and taking a time average of the motion along a closed energy trajectory infinitesimally close to the saddle energy trajectory. Thus, by dint of thermal fluctuations, the (noisy) trajectory (i.e., during a round trip of the well) may become the separatrix or the open trajectory on which the particle exits the well. Now the average, being *along a*

trajectory, is, of course, equivalent to an average over the fast phase variable. Thus, a diffusion equation in the slow energy (or action) variable emerges meaning of course that the purely streaming trajectories characteristic of the undamped motion that are governed by the single-particle Liouville equation now diffuse in energy space due to the action of the noise. Now, once again, the time derivative of the distribution function (when the latter is written as a function of the energy using the averaging procedure above) is *exponentially small* at the saddle point. Hence, the stationary solution in the energy variable may be used [3,4]. This procedure yields the Kramers' VLD formula (or energy-controlled diffusion rate)

$$\Gamma^{\text{VLD}} = \frac{\beta S(E_C)}{k_B T} \Gamma^{\text{TST}} = \frac{\omega_A}{2\pi} \frac{\beta S(E_C)}{k_B T} e^{-\Delta V} \quad (22)$$

This formula holds when in Eq. (19) $\mu \ll 1$, that is, $\beta S(E_C) \ll k_B T$ and unlike the TST result vanishes when $\beta \rightarrow 0$, so that escape is impossible without coupling to the bath. Thus, in all cases, analytical formulas for the escape rate rest on the fact that, in the relevant damping regimes, the Klein–Kramers equation may be reduced to an equation in a single coordinate.

In summary, the VLD formula demonstrates that escape is impossible in the absence of coupling to the bath. Likewise, if the coupling to the bath is very large, the escape rate vanishes. Kramers made several estimates of the range of validity of both IHD and VLD formulas and the intermediate (or moderate) damping (ID) regime where the TST Eq. (5) holds with a high degree of accuracy. He was, however, unable to give a formula in the underdamped regime lying between IHD and VLD, as there $\beta S(E_C) \approx k_B T$ so that no small perturbation parameter now exists. In essence, this problem, known as the Kramers turnover, essentially represents the interplay between purely energy and purely spatially controlled diffusion (when neither mechanism wholly dominates) and was solved in intuitive fashion nearly 50 years later by Mel'nikov [8] and Mel'nikov and Meshkov [10] and rigorously elaborated upon in Refs [12,29]. They constructed an integral equation for the evolution of the energy distribution function that they solved using the Wiener–Hopf method [3,30,31] and so obtained an escape rate formula that is valid for all values of the friction β , namely,

$$\Gamma = A(\Delta) \Gamma^{\text{IHD}} \quad (23)$$

where the Kramers dissipation parameter $\Delta = \beta S(E_C)/(k_B T)$ is the energy loss per cycle of a particle librating with energy equal to the barrier energy and

$$A(\Delta) = \exp \left(\frac{1}{2\pi} \int_{-\infty}^{\infty} \ln \left[1 - e^{-\Delta(\lambda^2 + 1/4)} \right] \frac{d\lambda}{\lambda^2 + 1/4} \right) \quad (24)$$

is called the depopulation factor [32] because the flow across the barrier leads to a depopulation of the upper energy regions in the well. Moreover, such a depletion effect dominates the escape rate for very weakly damped systems because the small coupling to the bath ensures substantial deviations from the Boltzmann distribution in the well [32].

2. Range of Validity of the IHD and VLD Formulas

The IHD escape rate Γ^{IHD} in the limit of vanishing friction becomes the TST result Eq. (5). Such behavior is, however, inconsistent [3] with the assumptions made in the derivation of Γ^{IHD} and instead this limit yielding Γ^{TST} should be termed intermediate damping. The correct formula is Eq. (19). Indeed

$$\Gamma^{\text{VLD}} = \frac{\beta S(E_C) \omega_A}{2\pi k_B T} e^{-\Delta V} \quad (25)$$

In order for Eq. (25) to hold, β must be small compared with ω_A (underdamping). If $\beta = 2\omega_A$, we have aperiodic damping, and we might expect that there would be a plentiful supply of particles near the point C, thus the escape rate would be described by the IHD formula. Kramers [15], however, confesses (cf. Fig. 2) that he was unable to extend Eq. (25) to values of β that were not small compared with $2\omega_A$, that is, in the *crossover (turnover) region* between VLD and IHD and *a fortiori* to the entire underdamped region.

The approximate formula, Eq. (25), for the escape rate in the VLD limit is useful for the formulation of a criterion in terms of the barrier height for the ranges of friction in which the VLD and IHD Kramers formulas are valid. Using as an approximation, the harmonic oscillator action $S_C = 2\pi \Delta V/\omega_A$, Eq. (25) becomes

$$\Gamma = \Gamma^{\text{VLD}} = \frac{\beta \Delta V}{k_B T} e^{-\Delta V} \quad (26)$$

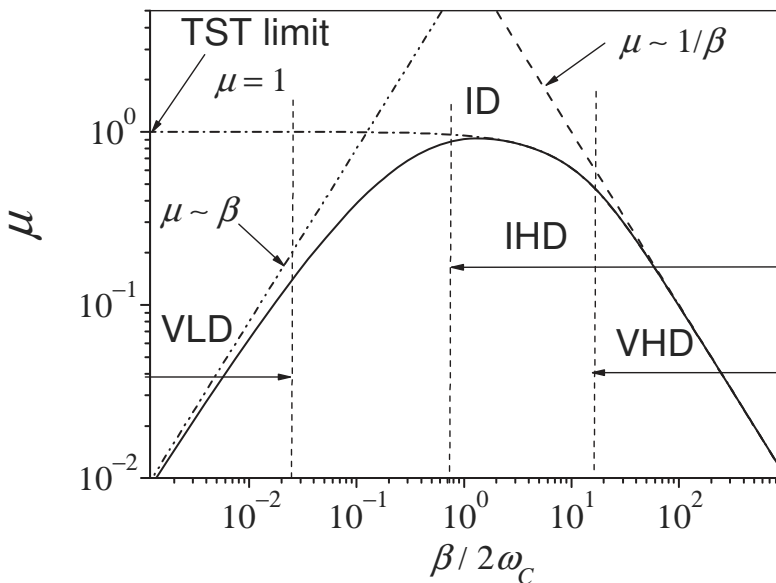


Figure 2. Diagram of damping regions for the prefactor μ in Eq. (19). Three regions exist, namely, VLD, intermediate damping (ID) (TST), and VHD, and two crossovers between them. Kramers' turnover refers to the underdamped region between ID and VLD.

Furthermore, if we define a dimensionless friction parameter $\alpha = 2\pi\beta/\omega_A$, Eq. (26) becomes

$$\Gamma = \frac{\alpha \Delta V}{k_B T} \Gamma^{\text{TST}} \quad (27)$$

so that $\alpha \Delta V$ is approximately the energy loss per cycle. Hence, the condition for the validity of the VLD Eq. (26) becomes $\alpha \Delta V \ll k_B T$, while one would expect the IHD formula to be valid if $\alpha \Delta V \geq k_B T$. The damping $\alpha \Delta V \approx k_B T$ defines the *crossover region*, where neither VLD nor IHD formulas are valid. This criterion serves to define the *Kramers turnover region* and is the reason behind the calculation of Mel'nikov and Meshkov mentioned above. We shall now give a physical interpretation of the three regions identified above.

We may summarize the existing results as follows. In the *mechanical* Kramers problem pertaining to point particles and by extension to rigid bodies, which all have separable and additive Hamiltonians, three regimes of damping appear:

- (i) *Intermediate to High Damping or Spatially Controlled Diffusion*. The general picture here [3] being that inside the well the distribution function is almost the Maxwell–Boltzmann distribution prevailing in the depths of the well. However, near the barrier it deviates from that equilibrium distribution due to the slow draining of particles across the barrier. The barrier region is so small in extent that one may approximate the potential in this region by an inverted parabola.
- (ii) *Very Low Damping or Energy-Controlled Diffusion*. Here, the damping is so small that the assumption involved in (i) namely that the particles approaching the barrier region have the Maxwell–Boltzmann distribution completely breaks down. Thus, the region where deviations from it occur extends far beyond the region where the potential may be approximated by an inverted parabola. Thus, we may now, by transforming the Klein–Kramers equation into energy and phase variables [by averaging over the phase and by supposing that the motion of a particle attempting to cross the barrier is almost conserved and is the librational motion in the well of a particle with energy equal to the barrier energy] obtain the escape rate. We remark that the assumption of almost conservative behavior (meaning that the energy loss per cycle is almost negligible and is equal to the friction times the action of the undamped motion at the barrier energy) ensures that the Liouville (conservative) term in the Klein–Kramers equation vanishes by the principle of conservation of density in phase. This is quite unlike IHD where strong coupling between the diffusion and the Liouville term exists. Thus, only the diffusion term in the energy variable remains (the dependence on the phase having been eliminated by averaging the

distribution in energy-phase variables along a *closed* trajectory of the energy since we assume a librational motion in the well).

- (iii) An intermediate (crossover) friction region and by extension almost the entire underdamped region, where neither IHD nor VLD formulas apply. Thus, none of the above approaches may be used. In contrast to the VLD case, the Liouville term in the Klein–Kramers equation does not now vanish, meaning that one cannot average out the phase dependence of the distribution function, which is ultimately taken account of by constructing from the Klein–Kramers equation a diffusion equation for the PDF with the energy and action as variables. This energy diffusion equation allows one to express the calculation of the energy distribution function at a given action, as a Fredholm integral equation that can be converted into one (or several) Wiener–Hopf equation(s) [3]. This procedure yields an integral equation for the depopulation factor, the product of which with the IHD escape rate [cf. Eq. (23)] provides an expression for the escape rate, which is valid for all values of the damping, so allowing the complete solution of Kramers’ problem. The depopulation factor derived from the Wiener–Hopf equation effectively allows for the coupling between the Liouville term and the dissipative term in the Klein–Kramers equation written in terms of energy–action variables, which is ignored in the VLD limit.

The Kramers theory may be verified numerically for high potential barriers by calculating the smallest nonvanishing eigenvalue of the Klein–Kramers equation [3]. This procedure is possible because of the exponential smallness of the escape rate, so that, in effect, that eigenvalue is very much smaller than all the higher order ones, which pertain to the fast motion inside the well. Thus, the Kramers escape rate is approximately given by the smallest nonvanishing eigenvalue if the barrier height ΔV is sufficiently large >5 . This method has been extensively used [14,16] to verify the Kramers theory, in particular its application to magnetic relaxation of single-domain ferromagnetic particles (see Section II.H). We shall now briefly summarize the extension of the spatially controlled diffusion Kramers theory to many dimensions due to Langer [13] as his calculations are fundamental both in the application of the Kramers theory to superparamagnetism and in the calculation of the quantum IHD rate.

3. *Extension of Kramers’ Theory to Many Dimensions in the IHD Limit*

The original IHD treatment of Kramers pertained to a mechanical system of one degree of freedom specified by the coordinate x with additive Hamiltonian $H = p^2/2m + V(x)$. Thus, the motion is separable and described by a 2D phase space with state variables (x, p) . However, this is not always so. For example, the motion of the magnetic moment in a single-domain ferromagnetic particle is

governed by a nonadditive and nonseparable Hamiltonian, which is simply the magnetocrystalline anisotropy energy of the particle. The Gilbert equation governing the relaxation process also causes *multiplicative noise* terms to appear, which complicates the calculations of the drift and diffusion coefficients in the Fokker–Planck equation (see [14]).

The phase space (librational) trajectories in the Kramers problem of the underdamped motion are approximately ellipses. The corresponding trajectories in the magnetic problem are much more complicated because of the nonseparable form of the energy. Similar considerations hold in the extension of the Debye theory of dielectric relaxation (see [14]) to include inertia as then one would usually (albeit with a separable Hamiltonian) have a six-dimensional phase space corresponding to the orientations and angular momenta of the rotator. These, and other considerations, suggest that the Kramers theory should be extended to a multidimensional phase space.

Such generalizations, having been instigated by Brinkman [33], were further developed by Landauer and Swanson [34]. However, the most complete treatment is due to Langer in 1969 [13], who considered the IHD limit. As specific examples of the application of the theory, we shall apply it to the Kramers IHD limit for particle and later to superparamagnets.

Before proceeding, we remark that a number of other interesting applications of the theory, which, as the reader will appreciate, is generally concerned with the nature of metastable states and the rates at which these states decay, have been mentioned by Langer [13] and we briefly summarize these. Examples are

1. A supersaturated vapor [35] that can be maintained in a metastable state for a very long time but that will eventually undergo condensation into the more stable liquid phase.
2. A ferromagnet, which can persist with its magnetization pointing in a direction opposite to that of an applied magnetic field.
3. In metallurgy, an almost identical problem occurs in the study of alloys whose components tend to separate on aging or annealing.
4. The final examples quoted by Langer are the theories of superfluidity and superconductivity, where states of nonzero superflow are metastable and so may undergo spontaneous transitions to states of lower current and greater stability.

According to Langer [13], all the phase transitions above take place via the nucleation and growth of some characteristic disturbance within the metastable system. Condensation of the supersaturated vapor is initiated by the formation of a sufficiently large droplet of the liquid. If this droplet is big enough, it will be more likely to grow than to dissipate and will bring about condensation of the entire sample. If the nucleating disturbance appears spontaneously as a thermodynamic

fluctuation it is said to be *homogeneous*. This is an intrinsic thermodynamic property of the system and is the type of disturbance described by Langer [13], which we shall summarize here. The other type of nucleation is *inhomogeneous nucleation* and occurs when the disturbance leading to the phase transition is caused by a foreign object, an irregularity, for example, in the walls of the container or some agent not part of the system of direct interest.

The above examples have been chosen in order to illustrate the breadth of applicability of the theory. For example, Langer's method, since it can be applied to a multidegree of freedom system, is likely to be of much use in calculating relaxation times for fine particle magnetic systems in which other types of interaction, such as exchange and dipole–dipole coupling, also appear. We also emphasize that Langer's treatment of the homogeneous nucleation problem contains within it the magnetic case of the Kramers' IHD calculation. The multidimensional Kramers problem was first solved in the VHD limit by Brinkman [33] and Landauer and Swanson [34], see also [3]. Also Langer's treatment constitutes the generalization of Becker and Döring's calculation [35] of the rate of condensation of a supersaturated vapor. A general discussion of this problem is given in Chapter 7 of Frenkel [36] on the kinetics of phase transitions.

4. Langer's Treatment of the IHD Limit

For easy comparison with previous work, we shall adopt the notation of Ref. [3]. Thus, we shall consider the Fokker–Planck equation for a multidimensional process governed by a state vector $\{\boldsymbol{\eta}\}$ that is [2,13]

$$\frac{\partial}{\partial t} \rho(\{\boldsymbol{\eta}\}, t) = \sum_{i=1}^{2N} \sum_{n=1}^{2N} \frac{\partial}{\partial \eta_i} M_{in} \left[\frac{\partial E}{\partial \eta_n} + k_B T \frac{\partial}{\partial \eta_n} \right] \rho(\{\boldsymbol{\eta}\}, t) \quad (28)$$

In Eq. (28), $E(\{\boldsymbol{\eta}\})$ is a Hamiltonian (energy) function having two minima at points A and B separated by a saddle point C surrounded by two wells. One, say that at B , is at a much lower energy than the other. The particles have to pass over the saddle point, which acts as a barrier at C . We again assume that the dimensionless barrier height $\Delta V = (E_C - E_A)/(k_B T)$ is very high (at least of the order of 5) so that the diffusion over the barrier is slow enough to ensure that a Maxwell–Boltzmann distribution is established and maintained near A at all times. The high barrier also assures that the contribution to the flux over the saddle point will come mainly from a small region around C . The $2N$ state variables $\{\boldsymbol{\eta}\} = \{\eta_1, \eta_2, \dots, \eta_{2N}\}$ are parameters, which could be the coordinates and momenta of a point in phase space or angular coordinates describing the orientation of the magnetization vector of a single-domain ferromagnetic particle. Generally, however, the first N of the η_i 's will be functions of the N coordinates of position [2]

$$\eta_i = \eta(x_i), \quad i = 1, 2, \dots, N \quad (29)$$

The second N of the η_i 's will be the conjugate momenta $\pi(x_i)$ taken at the same points:

$$\eta_{i+N} = \pi(x_i), \quad i = 1, 2, \dots, N \quad (30)$$

In fact, the η_i 's will often (although they need not) be the coordinates themselves; in which case (obviously) $\eta_i = x_i, i = 1, 2, \dots, N$. Here, when the noise term in the Langevin equation is ignored, the system evolves in accordance with the deterministic equation

$$\dot{\eta}_i = - \sum_n M_{in} \frac{\partial E}{\partial \eta_n} \quad (31)$$

where M_{ij} are the matrix elements of the transport matrix \mathbf{M} , which, for simplicity, we shall assume to be constant. An example of such a system is the translational Brownian motion of a particle in a potential in the IHD limit.

We may define the matrices \mathbf{D} and \mathbf{A} by the equations

$$\mathbf{D} = (\mathbf{M} + \mathbf{M}^T)/2 \quad (32)$$

and

$$\mathbf{A} = (\mathbf{M} - \mathbf{M}^T)/2 \quad (33)$$

where $\mathbf{M} = (M_{ij})$ is the *transport* matrix resulting from Eq. (31) and the symbol T means matrix transposition. The matrix \mathbf{D} is called the *diffusion* matrix, which characterizes the thermal fluctuations due to the heat bath while the matrix \mathbf{A} describes the motion in *the absence of the bath*, that is the inertial term in the case of mechanical particles, and if \mathbf{D} is not identically zero, then the dissipation of energy satisfies [2]

$$\dot{E} = - \sum_{i,n} \frac{\partial E}{\partial \eta_i} D_{in} \frac{\partial E}{\partial \eta_n} \leq 0 \quad (34)$$

We consider, as before, a single well and suppose that at finite temperatures a Maxwell–Boltzmann distribution is set up and the density at equilibrium is

$$\rho_{\text{eq}}(\{\boldsymbol{\eta}\}) = \frac{1}{Z} e^{-E(\{\boldsymbol{\eta}\})/(k_B T)} \quad (35)$$

where

$$Z \equiv \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} e^{-E/(k_B T)} d\eta_1 \dots d\eta_{2N} \quad (36)$$

is the partition function. The IHD escape rate for this multivariable problem may be calculated by the flux over population method.

We make the following assumptions about $\rho(\{\boldsymbol{\eta}\})$:

1. It obeys the stationary Fokker–Planck equation (i.e., $\dot{\rho} = 0$), which is (on linearization about the saddle point)

$$\sum_{i,n} \frac{\partial}{\partial \eta_i} M_{in} \left[\sum_k e_{nk} (\eta_k - \eta_k^S) + k_B T \frac{\partial}{\partial \eta_n} \right] \rho(\{\boldsymbol{\eta}\}) = 0 \quad (37)$$

where the e_{jk} are the coefficients in the Taylor expansion of the energy about the saddle point truncated at the second term, namely the quadratic (form) approximation

$$E(\{\boldsymbol{\eta}\}) = E_C - (1/2) \sum_{i,n} e_{in} (\eta_i - \eta_i^C) (\eta_n - \eta_n^C), \quad \{\boldsymbol{\eta}\} \approx \{\boldsymbol{\eta}^C\} \quad (38)$$

and E_C is the value of the energy function at the saddle point (compare Kramers' method above, there the saddle point is a one-dimensional maximum). Equation (38) constitutes the paraboloidal approximation to the potential in the vicinity of the saddle point. For example, in magnetic relaxation in a uniform field with uniaxial anisotropy, the energy surface in the vicinity of the saddle point will be a hyperbolic paraboloid [37]. Equation (37) is the multidimensional Fokker–Planck equation linearized in the region of the saddle point.

2. Due to the high barrier just as in the Kramers high damping problem, a Maxwell–Boltzmann distribution is set up in the vicinity of the bottom of the well, that is, at A , so

$$\dot{E} = - \sum_{i,n} \frac{\partial E}{\partial \eta_i} D_{in} \frac{\partial E}{\partial \eta_n} \leq 0 \quad (39)$$

$$\rho(\{\boldsymbol{\eta}\}) \approx \rho_{\text{eq}}(\{\boldsymbol{\eta}\}), \quad \{\boldsymbol{\eta}\} \approx \{\boldsymbol{\eta}^A\} \quad (40)$$

3. Practically, no particles have arrived at the far side of the saddle point so that we have the sink boundary condition

$$\rho(\{\boldsymbol{\eta}\}) = 0, \quad \{\boldsymbol{\eta}\} \text{ beyond } \{\boldsymbol{\eta}^C\} \quad (41)$$

This is Kramers' condition that only rare particles of the assembly cross the barrier. Just as the Klein–Kramers problem for one degree of freedom, we make the substitution

$$\rho(\{\boldsymbol{\eta}\}) = g(\{\boldsymbol{\eta}\}) \rho_{\text{eq}}(\{\boldsymbol{\eta}\}) \quad (42)$$

(the function g is known as the crossover function). Thus, we obtain from Eqs. (35) and (37) an equation for g , namely,

$$\sum_{i,n} M_{ni} \left[- \sum_k e_{nk} (\eta_k - \eta_k^C) - k_B T \frac{\partial}{\partial \eta_n} \right] \frac{\partial g}{\partial \eta_i} = 0 \quad (43)$$

where $\{\boldsymbol{\eta}\} \approx \{\boldsymbol{\eta}^C\}$. We postulate that g may be written in terms of a single variable u , namely,

$$g(u) = (2\pi k_B T)^{-1} \int_u^\infty e^{-z^2/(2k_B T)} dz \quad (44)$$

and we assume that u has the form of the linear combination

$$u = \sum_i U_i (\eta_i - \eta_i^C) \quad (45)$$

This is essentially Kramers' method of forcing the multidimensional Fokker–Planck equation into an equation in a single variable u (in his original case, a linear combination of the two variables, position and velocity, so that $u = p - ax'$). We must now determine the coefficients U_i of the linear combination u of the η_j . This is accomplished as follows. We define the matrix $\tilde{\mathbf{M}} = -\mathbf{M}^T$. Then we shall have the coefficients U_i of the linear combination as a solution of the *eigenvalue problem*

$$- \sum_{i,n} U_i \tilde{M}_{in} e_{nk} = \lambda_+ U_k \quad (46)$$

The eigenvalue λ_+ is the *deterministic growth rate of a small deviation from the saddle point*, and is the positive eigenvalue of the system matrix of the noiseless Langevin equations, linearized about the saddle point. It characterizes the unstable barrier-crossing mode. Thus, in order to calculate λ_+ , all that is required is a knowledge of the energy landscape and Eq. (46) need not in practice be involved. Equation (46) is obtained essentially by substituting the linear combination u , that is, Eq. (45), into Eq. (43) for the crossover function and requiring the resulting equation to be a proper ordinary differential equation in the single variable u with solution given by Eq. (44) (the details of this are given in Ref. [3]). Equation (46) may also be written in the matrix form

$$-\mathbf{U}^T \tilde{\mathbf{M}} \mathbf{E}^C = \lambda_+ \mathbf{U}^T \quad (47)$$

(Hänggi et al. [2] describe this equation by stating that \mathbf{U}^T is a “left eigenvector” of the matrix $-\tilde{\mathbf{M}}\mathbf{E}^C$. The usual eigenvalue equation of an arbitrary matrix \mathbf{A} is $\mathbf{A}\mathbf{X} = \lambda\mathbf{X}$. In the above terminology, \mathbf{X} would be a “right eigenvector” of \mathbf{A}). In Eq. (47), $\mathbf{E}^C \equiv (e_{ij})$ is the matrix of the second derivatives of the potential evaluated at the saddle point that is used in the Taylor expansion of the energy near the saddle point. The determinant of this (Hessian) matrix is the Hessian itself. The normalization of U_i is fixed so that

$$\lambda_+ = \sum_{i,n} U_i M_{in} U_n \quad (48)$$

which is equivalent to

$$\sum_{i,n} U_i e_{in}^{-1} U_n = -1 \quad (49)$$

This condition ensures that the crossover function, Eq. (44), retains the form of an error function and so may describe diffusion over a barrier. Alternatively, one may say that the foregoing conditions require that the entry in the diffusion matrix in the direction of flow (i.e., the unstable direction) is nonzero, that is, *we have current over the barrier and so particles escape the well.*

Now the Fokker–Planck equation (28) is a continuity equation for the representative points just as described earlier so that

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{J} = 0 \quad (50)$$

Thus by inspection, we find that the current density becomes

$$j_i = - \sum_n M_{in} \left[\frac{\partial E}{\partial \eta_n} + k_B T \frac{\partial}{\partial \eta_n} \right] \rho \quad (51)$$

and we obtain, using Eqs. (35), (43) and (44) for the *stationary* current density, that is, $\partial \rho / \partial t = 0$,

$$j_i(\{\eta\}) = \frac{1}{\sqrt{2\pi}} \sum_n M_{in} U_n \rho_{\text{eq}}(\{\boldsymbol{\eta}\}) e^{-u^2/(2k_B T)} \quad (52)$$

We now take advantage of the condition stated above that the flux over the barrier emanates from a small region around the saddle point C . We integrate the current density over a plane containing the saddle point but not parallel to the flow of

particles. The plane $u = 0$ will suffice here. The total current, that is, the flux of particles, is

$$J = \sum_i \int_{u=0} j_i(\{\boldsymbol{\eta}\}) dS_i \quad (53)$$

Using Eq. (53) with the quadratic approximation of Eq. (38) for the energy near the saddle point, the integration for the total flux (current) now yields after a long calculation [3]:

$$J \approx \frac{1}{2\pi Z} \sum_{i,j} U_i M_{ij} U_j \left| \sum_{i,j} U_i e_{ij}^{-1} U_j \det \left((2\pi k_B T)^{-1} \mathbf{E}^C \right) \right|^{-1/2} e^{-E_C/(k_B T)} \quad (54)$$

From Eqs. (48) and (49), we immediately obtain

$$J = \frac{\lambda_+}{2\pi Z} \left| \det \left((2\pi k_B T)^{-1} \mathbf{E}^C \right) \right|^{-1/2} e^{-E_C/(k_B T)} \quad (55)$$

Now, we assume that the energy function near the bottom of the well A may again be written in the quadratic approximation

$$E = E_A + \frac{1}{2} \sum_{i,j} a_{ij} \left(\eta_i - \eta_i^A \right) \left(\eta_j - \eta_j^A \right) \quad (56)$$

and we write $\mathbf{E}^A = (a_{ij})$ so that the number of particles in the well is [3]

$$n_A = \left\{ \det[(2\pi k_B T)^{-1} \mathbf{E}^A] \right\}^{-1/2} Z^{-1} \quad (57)$$

Now the escape rate Γ , by the usual flux over population method [1,2], is defined to be $\Gamma = J/n_A$ and so from Eqs. (55) and (57) in terms of the unique positive eigenvalue λ_+ of the set of *noiseless* Langevin equations linearized about the saddle point, we have

$$\Gamma = \frac{\lambda_+}{2\pi} \sqrt{\frac{\det\{\mathbf{E}^A\}}{|\det\{\mathbf{E}^C\}|}} e^{-(E_C - E_A)/(k_B T)} = \lambda_+ \frac{\omega_{A,0}}{2\pi} \left(\prod_{i=1}^N \omega_{A,i} / \prod_{i=1}^N \omega_{C,i} \right) e^{-\Delta V} \quad (58)$$

which is Langer's [13] expression in terms of the Hessians of the saddle and well energies for the escape rate for a multidimensional process in the IHD limit. The result again pertains to this limit because of our postulate that the potential in the vicinity of the saddle point may be approximated by the first two terms of its Taylor series. Thus, once again, Eq. (58) fails for very small damping because the region of deviation from the Maxwell–Boltzmann distribution prevailing in the depths of the well extends far beyond the narrow region at the top of the barrier in which the potential may be replaced by its quadratic approximation. In passing,

we remark that rate theory at weak friction is generally known as “unimolecular rate theory” [2] the VLD limit of Kramers treated earlier being an example of this. For a general discussion, see Ref. [2].

In addition with regard to Eq. (58), Langer obtained the imaginary part of the equilibrium free energy of a metastable state evaluated using steepest descents in terms of the Hessians of the saddle and well energies, namely,

$$\frac{\text{Im}J}{k_B T} = \frac{1}{2} \sqrt{\frac{\det\{\mathbf{E}^A\}}{|\det\{\mathbf{E}^C\}|}} e^{-\Delta V} \quad (59)$$

Hence, we have the important relation

$$\Gamma = \frac{\lambda_+}{\pi} \frac{\text{Im} J}{k_B T} \quad (60)$$

As well put by Hänggi et al. [2], the generalization of the Kramers rate due to Langer is then equivalent [cf. Eq. (6)] to a multidimensional TST rate where the dissipative motion is modeled in the entire phase space of the system, that is, one treats explicitly the coupling to the bath degrees of freedom as was accomplished by Pollak [18]. Thus, Langer’s expression is the TST rate in the complete phase space, that is, with all degrees of freedom included. We also remark that λ_+ the eigenvalue associated with the unstable barrier-crossing mode effectively represents a renormalized barrier frequency that is known [2] as the Grote–Hynes frequency.

5. *Kramers’ Formula as a Special Case of Langer’s Formula*

As an example of Langer’s method, we shall use it to derive the IHD result of Kramers. To recover the Kramers formula, Eq. (20), by Langer’s method, we take $N = 1$, thus the state variables are the position and momentum so that $\eta_1 = x$ and $\eta_2 = p$. The noiseless Langevin equations are

$$\dot{x} = \frac{p}{m}, \quad \dot{p} = -\beta p - \frac{dV}{dx} \quad (61)$$

Here, V denotes the potential energy and $\beta = \zeta/m$ is the friction coefficient. Because

$$\frac{\partial E}{\partial p} = \frac{p}{m}, \quad \frac{\partial E}{\partial x} = \frac{dV}{dx} \quad (62)$$

where $E = p^2/(2m) + V(x)$, Eq. (61) can be rewritten as

$$\dot{\eta}_1 = \frac{\partial E}{\partial \eta_2}, \quad \dot{\eta}_2 = -m\beta \frac{\partial E}{\partial \eta_2} - \frac{\partial E}{\partial \eta_1} \quad (63)$$

Hence, we have the equation of motion in terms of the state variables (η_1, η_2) of the general case of Langer's method above as

$$\begin{pmatrix} \dot{\eta}_1 \\ \dot{\eta}_2 \end{pmatrix} = - \begin{pmatrix} 0 & -1 \\ 1 & m\beta \end{pmatrix} \begin{pmatrix} \partial E / \partial \eta_1 \\ \partial E / \partial \eta_2 \end{pmatrix} \quad (64)$$

where the transport matrix \mathbf{M} is

$$\mathbf{M} = (M_{ij}) = \begin{pmatrix} 0 & -1 \\ 1 & m\beta \end{pmatrix} \quad (65)$$

Here, we can take the saddle point C as the origin, so $\eta_1^C = 0$ and $E_C = 0$. The momentum of a particle just escaping is zero also, so $\eta_2^C = 0$. Thus, we have the energy in the vicinity of the saddle point

$$E = -\frac{m\omega_C^2\eta_1^2}{2} + \frac{\eta_2^2}{2m} \quad (66)$$

We now determine λ_+ . We have from Eqs. (64) and (66) the linearized noiseless Langevin equation (which will have as general solution a linear combination of an exponentially growing mode and an exponentially decaying mode)

$$\begin{aligned} \begin{pmatrix} \dot{\eta}_1 \\ \dot{\eta}_2 \end{pmatrix} &= \begin{pmatrix} 0 & 1 \\ -1 & -m\beta \end{pmatrix} \begin{pmatrix} \partial E / \partial \eta_1 \\ \partial E / \partial \eta_2 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ -1 & -m\beta \end{pmatrix} \begin{pmatrix} -m\omega_C^2\eta_1 \\ \eta_2/m \end{pmatrix} \\ &= \begin{pmatrix} 0 & 1/m \\ m\omega_C^2 & -\beta \end{pmatrix} \begin{pmatrix} \eta_1 \\ \eta_2 \end{pmatrix} \end{aligned} \quad (67)$$

or

$$\dot{\boldsymbol{\eta}} = \mathbf{A}\boldsymbol{\eta}, \quad \mathbf{A} = \begin{pmatrix} 0 & 1/m \\ m\omega_C^2 & -\beta \end{pmatrix} \quad (68)$$

with secular equation

$$\det(\mathbf{A} - \lambda\mathbf{I}) = 0 \quad (69)$$

We, thus, solve the secular equation, namely, $\lambda(\lambda + \beta) - \omega_C^2 = 0$, to find

$$\lambda_{\pm} = \pm \sqrt{\omega_C^2 + \beta^2/4} - \beta/2 \quad (70)$$

We pick the upper sign so that the solution (which is now always positive) corresponds to the *unstable barrier-crossing mode*, hence

$$\lambda_+ = \sqrt{\omega_C^2 + \beta^2/4} - \beta/2 \quad (71)$$

Now the Hessian matrices of the saddle and well energies are given by

$$\mathbf{E}^C = \begin{pmatrix} m\omega_C^2 & 0 \\ 0 & -1/m \end{pmatrix} \quad \text{and} \quad \mathbf{E}^A = \begin{pmatrix} m\omega_A^2 & 0 \\ 0 & 1/m \end{pmatrix} \quad (72)$$

Thus, the Hessians are given by $\det\{\mathbf{E}^C\} = -\omega_C^2$ and $\det\{\mathbf{E}^A\} = \omega_A^2$ and so

$$\sqrt{|\det\{\mathbf{E}^A\}/\det\{\mathbf{E}^C\}|} = \omega_A/\omega_C \quad (73)$$

The escape rate is then

$$\Gamma = \frac{\lambda_+\omega_A}{2\pi\omega_C} e^{-\Delta V} = \frac{\omega_A}{2\pi} \left[\sqrt{1 + \frac{\beta^2}{4\omega_C^2}} - \frac{\beta}{2\omega_C} \right] e^{-\Delta V} \quad (74)$$

Equation (74) is Kramers' IHD Eq. (20). We will return to Langer's method when we discuss magnetic relaxation in Section II.H.

B. Kramers' Turnover Problem

We have briefly mentioned that the VLD Eq. (22) is of particular significance in that it clearly demonstrates that escape is impossible in the absence of coupling to the bath. Similarly, if the coupling to the bath is very large, the escape rate becomes zero. Kramers, in his original paper made several estimates of the range of validity of both IHD and VLD formulas and the region in which the TST theory embodied in Eq. (5) holds with a high degree of accuracy. We saw, however, that he was unable to give a formula in the Kramers turnover region between IHD and VLD, as there $\beta S(E_C) \approx k_B T$ so that no small perturbation parameter now exists. Here, the coupling between the Liouville and dissipative terms in the Klein–Kramers equation enters so that one may no longer ignore the Liouville term as was done in the very low damping regime. We also stated that this problem, named the Kramers turnover, was solved in *ad hoc* fashion nearly 50 years later by Mel'nikov and Meshkov [8,10]. They constructed an integral equation for the evolution of the energy distribution function in the vicinity of the separatrix that they solved using the Wiener–Hopf method [30,31] and so obtained a simple integral formula for the escape rate Γ bridging the VLD and IHD solutions. Now both the IHD and the VLD rates, already derived using two completely different approaches, are invalid in the Kramers turnover region and almost the entire

underdamped regime $\beta S(E_C) \leq k_B T$ between ID (TST) and VLD. The nomenclature *turnover* or *crossover* follows because in IHD the prefactor of the escape rate is inversely proportional to the damping β while in VLD, where the coupling between the dissipative and conservative terms in the Fokker–Planck equation is ignored, it is directly proportional to it (cf. Fig. 2). Thus, it is intuitively clear that the underdamped case requires its own mathematical technique accounting for the coupling between these terms [8,10]. This was initiated by Iche and Nozières [38] who showed that the Klein–Kramers equation can then be reduced to an integral equation. However, independently of them, Mel’nikov [8] (whose notation we shall adhere to as far as possible) also proposed the reduction of that equation to an integral equation in the energy variable with a Gaussian kernel with sole action parameter $\Delta = \beta S(E_C)/k_B T$. Thus, just as in VLD the underdamped Brownian particle moves in a potential well in an almost deterministic way, being only slightly perturbed by the stochastic forces [10]. The total energy of the particle is again the most slowly varying quantity and we require only the unperturbed trajectory corresponding to the absolute minimum energy needed to escape the well. We then consider *small perturbations of this undamped trajectory* due to thermal fluctuations.

The solution of the Kramers problem was then described in detail [8,10] both for single- and double-well potentials (see Hänggi et al. [2] and Coffey et al. [3] for reviews). For a single isolated well, the escape rate Γ is given by

$$\Gamma \sim \mu \Gamma^{\text{TST}} \quad (75)$$

where the prefactor μ is now given by

$$\mu = \left[\sqrt{1 + \beta^2/(2\omega_C)^2} - \beta/(2\omega_C) \right] A(\Delta) \quad (76)$$

The Kramers parameter $\Delta = \beta S(E_C)/k_B T$ is the ratio of the energy loss per cycle to the thermal energy of a librating particle with energy equal to the barrier energy, and $A(\Delta)$ is a depopulation factor interpolating between the VLD and ID damping regimes defined by Eq. (24). Thus, the coupling to the heat bath is absorbed into the two factors in μ while Γ^{TST} pertains to equilibrium properties of the system and does not require knowledge of the dynamics. Here, the depopulation factor $A(\Delta)$ effectively allows for the coupling between the Liouville and dissipative terms, which is ignored in the VLD limit. In the VLD limit, $\Delta \ll 1$, $A(\Delta) \rightarrow \Delta$ and so we regain the VLD escape rate while in the IHD limit $A(\Delta) \rightarrow 1$; thus, we ultimately regain the VHD escape rate using Eq. (75). For a double-well potential with two nonequivalent wells, the escape rate Γ is given by [10]

$$\Gamma \sim \left(\sqrt{1 + \frac{\beta^2}{4\omega_C^2}} - \frac{\beta}{2\omega_C} \right) \frac{A(\Delta_1)A(\Delta_2)}{A(\Delta_1 + \Delta_2)} \left(\Gamma_1^{\text{TST}} + \Gamma_2^{\text{TST}} \right) \quad (77)$$

where Δ_i is the ratio of the energy loss per cycle to the thermal energy of a librating particle having the barrier energy of well i and Γ_i^{TST} are the respective TST escape rates.

Equations (75) and (77) represent a complete solution of the Kramers turnover problem for an isolated and a double well, respectively. Everywhere they rely on the facts that one may rewrite the underdamped Klein–Kramers equation as a diffusion equation with the energy and action as independent variables and that the Green function is Gaussian. The energy distribution function for particles at various positions in a potential well can then be found in integral form by superposition. When complemented by boundary conditions, these integral relations can be converted into an integral equation for the energy distribution function for (potentially) escaping particles librating in a well at the barrier energy. The resulting one-sided convolution equation with a Gaussian kernel is solved by the Wiener–Hopf method [30,31] leading to an explicit expression for the escape rate in the underdamped case. Moreover, the precise shape of the potential well only enters the result via Δ that also governs the average energy of the escaping particles. It is then postulated that Eq. (75) that is valid for all damping regimes can be written down by simply taking the product of the depopulation factor and the Kramers IHD result. We remark that subsequently Grabert [29] and Pollak et al. [12] have presented a more rigorous solution of the Kramers turnover problem showing that Eq. (75) can be obtained without the *ad hoc* interpolation between the VLD and ID regimes (details in Section II.B.4) postulated by Mel’nikov and Meshkov [10].

Here, we shall indicate briefly how Eq. (75) may be derived and we shall demonstrate how the VLD result follows naturally from it. Thus, we shall first describe how the quasistationary Klein–Kramers equation, that is, with $\dot{\rho} = 0$, may for weak damping be transformed into an energy–action diffusion equation.

We again consider the simplest example of the metastable state when the Brownian particles having escaped over the barrier never return. The corresponding single-well potential $V(x)$ is shown in Fig. 3. We choose the zero of the potential to be the barrier top (so that E_C corresponds to $E = 0$) and as before the depth of the well is $\Delta V \gg 1$ while the boundary condition $\lim_{x \rightarrow \infty} \rho(p, x, t) = 0$ states that initially no particles exist at the far side of the barrier (cf. Fig. 3). Furthermore, the current of particles

$$J = m^{-1} \int_0^{\infty} p \rho(x, p, t) dp \quad (78)$$

calculated *near* the barrier top does not depend on x provided $|V(x)|/(k_B T) \ll \Delta V$. As before the conservation of the total number of particles of the ensemble (continuity equation) $\dot{N} = -J$ yields the connection between the lifetime $\tau = \Gamma^{-1}$

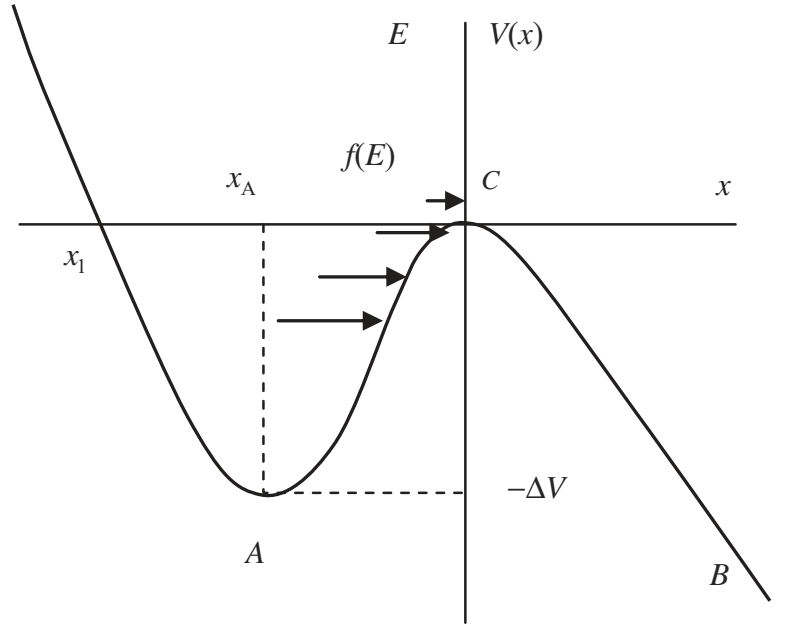


Figure 3. Escape from a single well.

of a particle in the well and the current. Normalizing the distribution ρ to one particle in the well, we have

$$\Gamma = J \quad (79)$$

which we shall use to calculate Γ . In accordance with Kramers, we shall assume that the flux over the barrier is due only to those particles having energy E in the *neighborhood* of the barrier top (i.e., the separatrix region). Moreover, $\Delta V \gg 1$ and the friction induced energy loss per cycle $\Delta \leq 1$. Hence just as in VLD, the total energy $E = p^2/(2m) + V(x)$ of a particle librating in the well is the most slowly varying quantity, so we use it as a new variable in the Klein–Kramers equation instead of the momentum while retaining the (relatively fast) position x that will later be subsumed in an action variable. Here, the relevant quantity is the quasistationary energy distribution function $f(E)$ of particles with a possibility of escaping because the decay rate $\Gamma = \tau^{-1}$ by the flux over population method is

$$\Gamma = J = \int_0^{\infty} f(E) dE \quad (80)$$

In effect $f(E)$ represents [2] the probability per unit time of finding a particle with energy E in the barrier region near a classical turning point of the trajectory in the well. Equation (80) follows from Eqs. (78) and (79) for the number of particles crossing the barrier in unit time, the fact that $dE = p dp/m$, and that in order for a particle to escape its momentum must be positive. Mel’nikov’s method [8] of calculation of $f(E)$ and $\Gamma = \tau^{-1}$ that relies on the conversion of the quasistationary Klein–Kramers equation in the barrier region to an equation in a single dependant variable is as follows.

1. Green Function of the Energy–Action Diffusion Equation

Mel’nikov’s procedure [8] for the evaluation of $f(E)$ unlike that used by Kramers in the VLD limit requires one to treat right- and left-going particles with respect to the barrier, denoted by the suffixes R, L separately. First we note that the quasistationary equation

$$\frac{dV}{dx} \frac{\partial \rho}{\partial p} - \frac{p}{m} \frac{\partial \rho}{\partial x} + \beta \frac{\partial}{\partial p} \left(\rho p + m k_B T \frac{\partial \rho}{\partial p} \right) = 0 \quad (81)$$

may be represented in terms of position–energy coordinates $\{x, E\}$ using the transformations (for a comprehensive discussion of such transformations see [16])

$$\frac{\partial}{\partial p} f_{R,L}(x, p) = \pm \sqrt{2[E - V(x)]/m} \frac{\partial}{\partial E} f_{R,L}(x, E) \quad (82)$$

$$\frac{\partial}{\partial x} f_{R,L}(x, p) = \frac{\partial}{\partial x} f_{R,L}(x, E) + \frac{dV}{dx} \frac{\partial}{\partial E} f_{R,L}(x, E) \quad (83)$$

where we define the distribution functions for the right- and left-going particles as

$$f_R = \rho(x, p) = \rho \left(x, \sqrt{2m[E - V(x)]} \right)$$

and

$$f_L = \rho(x, -p) = \rho \left(x, -\sqrt{2m[E - V(x)]} \right)$$

Furthermore, we can set $E = 0$ in the relationship

$$p(x, E) = \pm \sqrt{2m[E - V(x)]} \approx p(x, 0) = \pm \sqrt{-2mV(x)} \quad (84)$$

because we have chosen the separatrix trajectory to effectively coincide with $E = 0$ (see Fig. 3) and we suppose that the leading contributions to the escape stem from particles on trajectories very close to it in a *narrow* range of energy (skin) of order $k_B T$. Consider now the dissipative term in Eq. (81), namely,

$$\beta \frac{\partial}{\partial p} \left(\rho p + m k_B T \frac{\partial \rho}{\partial p} \right) \approx \frac{\beta p^2(x, 0)}{m} \frac{\partial}{\partial E} \left[\rho + k_B T \frac{\partial \rho}{\partial E} \right] \quad (85)$$

where we have used Eq. (84). Thus, the quasistationary equation (81) becomes

$$\frac{p}{m} \frac{\partial \rho}{\partial x} - \frac{dV}{dx} \frac{\partial \rho}{\partial p} = \frac{\beta}{m} p^2(x, 0) \frac{\partial}{\partial E} \left(\rho + k_B T \frac{\partial \rho}{\partial E} \right) \quad (86)$$

or in terms of $f_{R,L}(x, E)$ we now have the one-dimensional diffusion equation

$$\frac{\partial f_{R,L}}{\partial x} = \pm \beta \sqrt{-2mV(x)} \frac{\partial}{\partial E} \left(f_{R,L} + k_B T \frac{\partial f_{R,L}}{\partial E} \right) \quad (87)$$

Now we define the action $S(E) = \oint_E p dx$, where E denotes a closed contour with energy E , pertaining to librational motion in the well via

$$\frac{dS}{dx} = \pm \sqrt{2m [E - V(x)]} \approx \pm \sqrt{-2mV(x)} \quad (88)$$

recalling that inside the well $V(x)$ is negative since the top of the well corresponds to the zero of potential. Hence, Eq. (86) can be compactly represented as the energy–action diffusion equation

$$\frac{\partial f_{R,L}}{\partial S} = \beta \frac{\partial}{\partial E} \left(f_{R,L} + k_B T \frac{\partial f_{R,L}}{\partial E} \right) \quad (89)$$

describing diffusion and uniform drift in energy space in the separatrix region and so governing the noisy motion there. We remark that the notion of diffusion of energy trajectories as a function of action is already explicit in the work of Kramers.

The solution of Eq. (89) can be reduced to an integral equation using the principle of superposition by first determining the Green function $g(E, S|E', 0) \equiv g(E - E', S)$ (the transition probability in energy space). The Green function g is the solution of the equation

$$\frac{\partial g}{\partial S} = \beta \frac{\partial}{\partial E} \left(g + k_B T \frac{\partial g}{\partial E} \right) \quad (90)$$

subject to the initial condition $g(E, 0|E', 0) = \delta(E - E')$ [here we have dropped the subscripts R, L, writing $f_{R,L} = g$]. Defining the characteristic function $\tilde{g}(\lambda, S)$ by

$$\tilde{g}(\lambda, S) = \int_{-\infty}^{\infty} g(E - E', S) e^{i\lambda(E - E')/(k_B T)} d(E - E') \quad (91)$$

where the random variable $E - E'$ denotes the alteration in energy during a round trip (cycle) in the well, we have

$$\tilde{g}(\lambda, S) = \exp \left[-\beta S \lambda (\lambda + i) / (k_B T) \right] \quad (92)$$

Furthermore, at $\lambda - i/2$, \tilde{g} is real, namely,

$$\tilde{g}(\lambda - i/2, S) = \exp \left[-\beta S (\lambda^2 + 1/4) / (k_B T) \right] \quad (93)$$

Thus, the Green function g that represents the conditional probability that a particle leaving the barrier region with energy E' will return to it with energy E is given by [2]

$$g(E - E', S) = (4\pi\beta k_B TS)^{-1/2} \exp \left[-\frac{(E - E' + \beta S)^2}{4\beta k_B TS} \right] \quad (94)$$

Equation (94) follows almost from intuitive considerations because for extremely weak damping the conditional PDF g is strongly peaked around $E \sim E'$ due to the small loss of energy on the noisy trajectory infinitesimally close to the undamped deterministic librational trajectory [2]. The solution of Eq. (89) for an arbitrary initial distribution of energy $f(E', 0)$ is then given by the convolution integral

$$f(E, S) = \int_{-\infty}^{\infty} f(E', 0) g(E - E', S) dE' \quad (95)$$

2. Integral Equation for the Distribution Function in Energy–Action Variables

Now in order to derive a closed integral equation for the distribution function (population of escaping particles), we need additional information concerning $V(x)$ outside the barrier. By hypothesis these particles having surmounted the barrier never return. Thus, in terms of the functions $f_{R,L}(E, x)$, we have outside the well, that is, for $E > 0$ (because $E = 0$ defines the boundary of the well)

$$f_L(E, 0) = 0 \quad (96)$$

Conversely, close to the barrier the flux of left-going particles is simply due to right-going particles with $E < 0$ reflected from the barrier so that inside the well, that is, for $E < 0$

$$f_L[E, x(E)] = f_R[E, x(E)] \quad (97)$$

Here, $x(E)$ is the root of the equation of the separatrix $V(x) = E$, $x_1 < x < 0$ corresponding of course to the right-hand turning point at a given energy E . Equations (96) and (97) constitute boundary conditions because (a) they relate f_L to f_R for $E < 0$, (b) no left-going particles exist directly at the barrier top. Clearly particles with different values of E are reflected at different values of position $x(E)$. However, for $E \approx k_B T$ (the order of magnitude of a fluctuation), *the variation in the values of $x(E)$ is small in size compared to the overall extent of the well* in other words the separatrix region is thin. Hence, one may assume that all such particles propagate along (boundary layer) trajectories very close to the separatrix

$E = E_C = 0$. Thus, they can be described by the Green function (94) with $S = S(0)$ denoting the action per cycle of a particle librating in the well with energy equal to the barrier energy, namely,

$$S(0) \approx \int_{E_C} \sqrt{-2mV(x)} dx = 2 \int_{x_1}^0 \sqrt{-2mV(x)} dx \quad (98)$$

where E_C now indicates that the line integral is to be taken along the separatrix (which of course constitutes [14] an *open* trajectory rather than the closed trajectories of the librational motion in the well). The action $S(0)$ is the basic parameter of the problem and has already appeared in our discussion of the VLD result. The justification that $S(0)$ may be used can be given as follows. We have if $|E|/(k_B T) \ll \Delta V$ (details of the lemma are given in Ref. [3])

$$S(0) - S(E) = |E/\omega_C| \ln |k_B T \Delta V/E|$$

where ω_C is the barrier frequency. This expression tends to zero in the limit of small E .

We now return to the boundary conditions (96) and (97) and introduce following Mel'nikov [8] the new function

$$f(E) = f_R(E, 0), \quad E > 0, \quad f(E) = f_R[E, x(E)], \quad E < 0 \quad (99)$$

with $x(E)$ defined by the separatrix $E = E_C = 0$. Clearly $f(E)$ governs the escape rate for $E > 0$ and the rate of reflection at the barrier for $E < 0$. Now the reflected particles constitute a distribution of left-going particles f_L . They flow to the left-hand boundary of the well and are then reflected, thus f_L becomes f_R . They then flow across the well once more and reproduce the distribution $f(E)$. This is the condition that must accompany the integral equation (95) in order that it should become a *closed* integral equation for $f(E)$. Clearly the evolution of the energy distribution function in the *vicinity of the separatrix* is governed by the Green function

$$g(E - E', S) = (4\pi k_B T \delta)^{-1/2} e^{-(E - E' + \delta)^2 / (4k_B T \delta)} \quad (100)$$

where $\delta = \beta S(0)$ is the energy loss in one cycle (i.e., per oscillation) of the librational motion in the well with energy equal to the barrier energy. We can now write down by superposition our fundamental integral equation for the energy distribu-

tion function $f(E)$ or population of particles with a possibility of escaping in the form of the Wiener–Hopf equation [30,31]

$$f(E) = \int_{-\infty}^0 g(E - E') f(E') dE' \quad (101)$$

where $g(E - E') = g(E - E', S)$. Note that because the exponential factor in $g(E - E')$ decays so quickly we suffer no great error in replacing the lower limit by $-\infty$. This is important as otherwise the problem could not be posed as a Wiener–Hopf equation. Furthermore, we have the boundary condition that deep in the well $f(E)$ must become the Maxwell–Boltzmann distribution, that is,

$$f(E) = f_0(E) = \frac{\omega_A}{2\pi k_B T} e^{(-E/(k_B T)) - \Delta V} \quad (102)$$

(here, we have noted that $E \approx -k_B T \Delta V + \omega_A^2 (x - x_A)^2 / 2$ near x_A). Solving Eq. (101) for $f(E)$ yields from Eq. (80), the escape rate Γ effectively reducing to the calculation of the depopulation factor $A(\Delta)$ expressing the fact that the density at the barrier is no longer zero.

In order to evaluate $A(\Delta)$, we consider the Fourier transforms $\varphi^+(\lambda)$ and $\varphi^-(\lambda)$ defined as (so that λ is dimensionless)

$$\varphi^\pm(\lambda) = (2\pi/\omega_A) e^{\Delta V} \int_{-\infty}^{\infty} U(\pm E) f(E) e^{(i\lambda E)/(k_B T)} dE \quad (103)$$

where $U(x)$ is Heaviside's theta or step function. The functions $\varphi^+(\lambda)$ and $\varphi^-(\lambda)$, which are the Fourier transforms of $f(E)$ for $E > 0$ and $E < 0$, are analytical in the upper and lower complex half-planes of λ with the only exception being the pole of $\varphi^-(\lambda)$ at $\lambda = -i$. Using the boundary condition of a Maxwell–Boltzmann distribution deep in the well, that is, Eq. (102), one may then approximate $\varphi^-(\lambda)$ for $|\lambda + i| \ll 1$ as

$$\varphi^-(\lambda) \approx -i/(\lambda + i) \quad (104)$$

Clearly

$$\varphi^+(0) = \frac{2\pi}{\omega_A} e^{\Delta V} \int_0^{\infty} f(E) dE = \frac{2\pi}{\omega_A} \Gamma e^{\Delta V} \quad (105)$$

while by definition, cf. Eq. (80), in the underdamped region, where the prefactor $\mu \approx A$, the escape rate Γ is given by

$$\Gamma \approx A \frac{\omega_A}{2\pi} e^{-\Delta V} \quad (106)$$

On comparing Eqs. (105) and (106), the prefactor A is

$$A = \varphi^+(0) \quad (107)$$

which shows how the depopulation factor may be determined from the characteristic function of the energy distribution in the upper half-plane.

Now, with Eqs. (101) and (103), we have writing the Green function explicitly and using the properties of Gaussian integrals

$$\begin{aligned} \varphi^-(\lambda) + \varphi^+(\lambda) &= \frac{2\pi}{\omega_A} e^{\Delta V} \int_{-\infty}^0 \int_{-\infty}^{\infty} \frac{f(E')}{\sqrt{4k_B T \beta s}} e^{-((E-E'+\beta s)^2/(4k_B T \beta s))} e^{(i\lambda E)/k_B T} dE dE' \\ &= \frac{2\pi}{\omega_A} e^{\Delta V} e^{-((\lambda(\lambda+i)\beta s)/k_B T)} \int_{-\infty}^0 f(E') e^{(i\lambda E')/k_B T} dE' = \tilde{g}(\lambda) \varphi^-(\lambda) \end{aligned} \quad (108)$$

where $\tilde{g}(\lambda)$ is given by Eq. (92).

In order to illustrate [8] how the Wiener–Hopf method [30,31] may be used to determine $A = \varphi^+(0)$, we rewrite Eq. (108) as

$$\varphi^+(\lambda) + G(\lambda)\varphi^-(\lambda) = 0 \quad (109)$$

where $G(\lambda) = 1 - \tilde{g}(\lambda)$. The solution of Eq. (109) may now be determined in terms of $G(\lambda)$ as follows. We have from Eq. (109)

$$\ln [-\varphi^+(\lambda)] = \ln \varphi^-(\lambda) + \ln G(\lambda) \quad (110)$$

Next using Cauchy's integral formula, we define two functions $\ln G^+(\lambda)$ and $\ln G^-(\lambda)$ as

$$\ln G^\pm(\lambda) = \pm \frac{1}{2\pi i} \lim_{\varepsilon \rightarrow 0} \int_{-\infty}^{\infty} \frac{\ln G(\lambda')}{\lambda' - \lambda \mp i\varepsilon} d\lambda' \quad (111)$$

Both $G^+(\lambda)$ and $G^-(\lambda)$ are entire functions that have no zeros in the corresponding half-planes $\text{Im } \lambda > 0$ and $\text{Im } \lambda < 0$. Moreover, both $G^+(\lambda)$ and $G^-(\lambda) \rightarrow 1$ as $\lambda \rightarrow \infty$ and $G(\lambda)$ may be decomposed as

$$\ln G(\lambda) = \ln G^+(\lambda) + \ln G^-(\lambda) \quad (112)$$

or $G(\lambda) = G^+(\lambda)G^-(\lambda)$, so Eq. (109) may be rewritten as

$$\ln [-\varphi^+(\lambda)/G^+(\lambda)] = \ln [\varphi^-(\lambda)G^-(\lambda)] \quad (113)$$

As the functions on both sides of Eq. (113) are analytical in the two *different* half-planes of λ , both sides must be equal to an *entire* function that can be chosen to satisfy the boundary condition Eq. (104) and that may be taken as $\ln h(\lambda)$ so that

$$\varphi^+(\lambda) = -h(\lambda)G^+(\lambda) \quad \text{and} \quad \varphi^-(\lambda) = h(\lambda)/G^-(\lambda) \quad (114)$$

Now from Eq. (104), we have

$$h(\lambda) = -iG^-(-i)/(\lambda + i) \quad (115)$$

yielding with Eqs. (114) the solution of the Wiener–Hopf equation (113), namely,

$$\varphi^+(\lambda) = \frac{iG^+(\lambda)G^-(-i)}{\lambda + i} \quad \text{and} \quad \varphi^-(\lambda) = -\frac{iG^-(-i)}{G^-(\lambda)(\lambda + i)} \quad (116)$$

Thus, the prefactor $A = \varphi^+(0)$ is given by

$$A = G^+(0)G^-(-i) = |G^+(0)|^2 \quad (117)$$

since $G^-(-i) = [G^+(0)]^*$ (the asterisk denotes the complex conjugate). This can be verified by displacement of the contour of integration in Eq. (111) to the straight line $\text{Im } \lambda = -i/2$. Thus, we have with the replacement $\lambda' \rightarrow \bar{\lambda} - i/2$ in Eq. (111)

$$\ln G^+(0) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{\ln G(\bar{\lambda} - i/2)}{\bar{\lambda} - i/2} d\bar{\lambda} \quad (118)$$

where the shifted function

$$G(\bar{\lambda} - i/2) = 1 - \tilde{g}(\bar{\lambda} - i/2) = 1 - e^{-\Delta(\bar{\lambda}^2 + 1/4)}$$

is real [cf. Eq. (93)]. Thus using Eq. (118), we obtain the depopulation factor Eq. (24), namely,

$$A(\Delta) = |G^+(0)|^2 = e^{\frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{\ln \{1 - \exp[-\Delta(\lambda^2 + 1/4)]\}}{\lambda^2 + 1/4} d\lambda} \quad (119)$$

One can show (details in Ref. [3]) that

$$A(\Delta) \sim \Delta \quad \text{for } \Delta \ll 1 \quad \text{and} \quad A(\Delta) \rightarrow 1 \quad \text{for } \Delta \gg 1 \quad (120)$$

so regaining the VLD and IHD results, respectively.

3. Kramers' VLD Result

Before proceeding, it will be instructive to present a method of regaining the VLD result, Eq. (22) alternative to that of Kramers. In the VLD limit, the integral equation (101) reduces to the differential equation

$$\delta \partial_E (f + k_B T \partial_E f) = 0, \quad \delta \ll k_B T \quad (121)$$

subject to the boundary condition $f(0) = 0$. The reduction may be accomplished by noting that the derivative $f'(E)$ satisfies the same integral Eq. (101) as $f(E)$ itself [8] (see also [39]).

We now determine $f(E)$ from Eq. (121) and then use it to calculate the VLD escape rate. We have

$$f + k_B T \partial_E f = C' \quad (122)$$

where C' is a constant to be determined. Because deep in the well we have the Maxwell–Boltzmann distribution (102), the complete solution of Eq. (122) is

$$f(E) = \frac{\omega_A}{2\pi k_B T} e^{-\Delta V - E/(k_B T)} + C' \quad (123)$$

We now stipulate that the boundary condition at the top of the well is $f(0) = 0$. Thus, $C' = -(\omega_A/2\pi k_B T) \exp(-\Delta V)$ yielding

$$f(E) = \frac{\omega_A}{2\pi k_B T} \left[e^{-E/(k_B T)} - 1 \right] e^{-\Delta V/(k_B T)} \quad (124)$$

The condition that the density of particles vanishes at the top of the barrier is tantamount (cf. [40]) to ignoring the time to go from the critical or barrier energy trajectory to the separatrix. Put more succinctly the 50/50 chance of the particle returning to the well is replaced by zero chance of returning in VLD only. Thus, in VLD *only*, all particles are absorbed at the barrier. This condition of complete depopulation at the barrier is also used by Kramers when he explicitly imposes $(\rho e^{E/(k_B T)})_C \approx 0$. It must be justified rigorously as shown by Mel'nikov [8] who by calculating the average energy of the escaping particles deduced that $f(0) \sim \omega_A \delta (k_B T)^{-2} \exp(-\Delta V)$ that is negligible only in the VLD case. Now in order to get the VLD escape rate from Eq. (121), we have to evaluate the current at the barrier J , which is defined as

$$f\delta + k_B T \delta \partial_E f = -J \quad (125)$$

Now at the barrier top $E = 0$, $f(0) = 0$ so that $J = -k_B T \delta \partial_E f = \Gamma$, since we have normalized to one particle in the well. Thus noting Eq. (124), we have the Kramers VLD result, Eq. (22), that is perhaps a more convincing derivation than that of Kramers.

4. Criticisms of the Ad Hoc Approach of Mel'nikov and Meshkov

The original calculations of Kramers have the disadvantage that the transmission factor is determined by essentially two separate approaches that are valid for very weak and high damping, respectively [29]. The results are then combined in an *ad hoc* fashion to yield an interpolation formula valid in the entire range of damping cf. Eqs. (23) and (24). Thus, it was realized by Grabert [29] and Pollak et al. [12] that a unified treatment of the Kramers turnover problem was lacking.

Such a unified theory effectively initiated by Grabert is based on a normal mode approach to dissipative dynamics that has its origin in the generalized Langevin equation for the coordinate q , namely,

$$M\ddot{q} + \int_0^t \eta(t-t')\dot{q}(t')dt' + \frac{\partial V}{\partial q} = F(t) \quad (126)$$

Here, the system coordinate q of effective mass M moves in a potential $V(q)$, experiences a friction kernel $\eta(t)$ and a random force $F(t)$, that originates from the thermal motion of the liquid. The force $F(t)$ is Gaussian and satisfies the second fluctuation dissipation theorem

$$\langle F(t)F(0) \rangle = k_B T \eta(t)$$

Kramers treated the problem in the Markovian limit, that is, $\eta(t) = 2M\beta\delta(t)$, where β is the static friction parameter usually taken to be proportional to the viscosity of the fluid. The unified theory proposed by Grabert [29] and Pollak et al. [12] is based on the normal mode approach to the dissipative dynamics described by the generalized Langevin equation that may be described in two steps. The first of these, as shown by Zwanzig [4,41], is to transform the generalized Langevin equation into a Hamiltonian where the system is linearly coupled to a bath of harmonic oscillators, that is, a transmission line. The second step [18,42,43] is a transformation of the coordinates of the Hamiltonian to normal modes. Then at a barrier one may uniquely identify the unstable normal mode associated with the barrier crossing [13]. At energies close to the barrier height the normal mode dynamics are virtually exact [18,21]. Hence, a multidimensional TST in the normal mode coordinates can be used and is equivalent to the spatial diffusion limited or IHD rate. The calculations leading to this result will be given later when we discuss the quantum IHD rate. The nub of the approach of Pollak [18,21] and Pollak et al. [12] is that the unstable normal mode decouples from the other modes very near to the barrier allowing one to describe the problem by a single degree of freedom stochastic process for the energy loss in the unstable normal mode. This immediately yields the escape rate that is very similar to that obtained by Mel'nikov and Meshkov [8,10]. However, two vital differences must be emphasized, namely,

the theory of Grabert [29] and Pollak et al. [12] deals with the *unstable normal mode energy along the reaction and not the physical configuration coordinate*. Second, the theory is formulated for arbitrary (non-Ohmic) friction, so that it is identical to that of Mel'nikov and Meshkov [8,10] only in the weak coupling limit. However, it goes smoothly without any *ad hoc* assumptions to the correct spatial diffusion IHD limit that is synonymous with the multidimensional TST limit and of course with Ohmic damping being assumed. Specifically speaking the loss of energy ΔE in the *unstable normal mode* now determines [2] the conditional probability $g(E|E')dE$ (assuming high barriers) that a system leaving the barrier region E' in the *unstable mode* returns to the barrier with an energy lying between E and $E + dE$. Hence, as before recalling that all calculations pertain to the barrier region [2], the probability $f(E)$ of finding the system in a region lying between energy E and $E + dE$ in the unstable normal mode, near a classical turning point is given by the integral equation

$$f(E) = \int_0^{E_C} g(E | E') f(E') dE' \quad (127)$$

Furthermore, as $E \rightarrow \infty$, $f(E) \rightarrow 0$ so that we may extend the domain of integration to infinity while deep in the well, that is, $E/E_C \ll 1$, $f(E)$ has the equilibrium value (note the difference with Eq. (90) of [10])

$$f_{\text{eq}}(E) = \frac{\omega_A \lambda^+}{2\pi \omega_C k_B T} e^{-E/(k_B T)} \quad (128)$$

where λ^+ , which denotes the unstable normal mode angular frequency, is given by (the Grote-Hynes frequency)

$$\lambda^+ = \left(\omega_C^2 + \tilde{\eta}^2/4 \right)^{1/2} - \tilde{\eta}/2 \quad (129)$$

where $\tilde{\eta}$ represents the Laplace transform of the friction kernel $\eta(t)$ in the generalized Langevin equation. Thus, in the approach of the unstable normal mode the TST for linear coupling to a bath of harmonic oscillators [12] and so the dissipation is essentially involved in the *equilibrium distribution for the energy in the unstable barrier-crossing mode* and so in the boundary condition for Eq. (127). The escape rate in terms of $f(E)$ is as before

$$\Gamma = \int_{E_C}^{\infty} f(E) dE = \int_0^{\infty} f(E) dE \quad (130)$$

since E_C is zero for the isolated well configuration considered by Meshkov and Mel'nikov. Their procedure then yields in the notation of [12]

$$\Gamma = \frac{\omega_A}{2\pi} e^{-E_C/(k_B T)} \frac{\lambda^+}{\omega_C} \exp \left(\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{dy}{1+y^2} \ln \left[1 - e^{-\Delta(1+y^2)/4} \right] \right) \quad (131)$$

where Δ now denotes the dimensionless energy loss associated with the unstable normal mode coordinate that unlike in Ref. [10] does not in general coincide with the energy loss along the physical particle coordinate. For $\Delta \gg 1$, Γ reduces to the multidimensional TST value as incorporated in the boundary condition for $f(E)$, namely,

$$\Gamma = \frac{\omega_A}{2\pi} \frac{\lambda^+}{\omega_C} e^{-E_C/(k_B T)} \quad (132)$$

On the other hand, for Δ of the order of unity or smaller [2] the probability $f(E)$ per unit time now contains nonequilibrium effects giving rise to a transmission factor <1 that is below that of the multidimensional TST value. Moreover, for very low damping

$$\Gamma = \Gamma_{\text{VLD}} = \Gamma_{\text{TST}} \frac{\Delta}{k_B T} \quad (133)$$

which reduces for the original Kramers model (Ohmic friction) to $\Delta = \beta S(E_C)$, that is, the energy-controlled diffusion result.

C. Applications of the Theory of Brownian Movement in a Potential and of the Kramers Theory

Among the physical phenomena to which the theory has been applied are as follows:

1. Current–voltage characteristics of the Josephson junction.
2. Mobility of superionic conductors.
3. Dielectric and Kerr-effect relaxation in liquids and nematic liquid crystals.
4. Linewidths in nuclear magnetic resonance.
5. Incoherent scattering of slow neutrons.
6. Cycle slips in second-order phase-locked loops.
7. Quantum noise in ring-laser gyroscopes.
8. Thermalization of neutrons in a heavy gas moderator.
9. Photoelectromotive force in semiconductors.
10. Rate coefficient in chemical reactions.

11. Line shape of single mode semiconductor lasers.
12. Dynamics of a charged density wave condensate.
13. Dynamic light scattering.
14. Superparamagnetism (magnetization relaxation of nanoparticles).
15. Magnetic relaxation in ferrofluids.
16. Polymer dynamics.
17. Fluorescence depolarization,
18. Thermal noise in electrical circuits,
19. Diffusion magnetic resonance imaging, and so on.

For illustration, we shall consider below, as particular examples, the rotational Brownian motion of a single axis rotator in a symmetrical and asymmetrical double-well potential and the translational Brownian motion of a particle in a symmetrical double-well and tilted periodic potential. Despite the assumptions made, these simple models enable one to understand the physics of diffusion, relaxation, and resonance in nonlinear stochastic systems.

D. Escape Rate for a Fixed Axis Rotator in a Double-Well Potential

1. Turnover Formula for the Escape Rate for Fixed Axis Rotation

The Brownian motion in a periodic potential is of interest in a multitude of physical problems involving a relaxation process. Among the most prominent of these are dielectric relaxation and the dynamic Kerr effect of nematic liquid crystals, magnetic relaxation of single-domain ferromagnetic particles, dynamic response of Josephson tunneling junctions, transport phenomena in semiconductors, and so on [14,16,44]

Now this chapter is concerned with one of the most important characteristics associated with the Brownian motion in a potential well, namely, the longest relaxation time or the time required to escape the well. The longest relaxation time is essentially the inverse of the smallest nonvanishing eigenvalue λ_1 of the characteristic equation or secular determinant of the relevant dynamical system. Moreover, if the overbarrier mode characterized by λ_1 dominates the relaxation process as is always so for symmetrical potential wells, the escape time (λ_1^{-1}) will be closely approximated in the high-barrier limit by the integral relaxation time. This time is the area under the relaxation function of the appropriate dynamical variable [14]. In linear response, the integral relaxation time is identical to the correlation time of the corresponding autocorrelation function. However, for *asymmetrical* potentials such as those arising from the imposition of a strong external field, it is not always possible to identify the integral relaxation time with the escape time [14]. As far as the calculation of λ_1 is concerned, the secular equation may be

generated by averaging the appropriate Langevin equation over its realizations yielding the differential–recurrence equations governing the decay functions of the system (which is analogous to the use of matrix mechanics in quantum theory). Alternatively, one may expand the solution of the associated probability density diffusion equation (usually the specialized form of the Fokker–Planck equation known as the Klein–Kramers equation that applies to separable and additive Hamiltonians) in Fourier series in the position and velocity variables [14,16]. In each of the two methods, the secular determinant results from truncation of the set of differential–recurrence relations at a number large enough to achieve convergence of the resulting set of simultaneous ordinary differential equations. Alternatively, if the problem is represented in the frequency domain so that the more powerful continued fraction method may be used (which is very effective from a computational point of view), many convergents must be taken [16,45]. Thus, the smallest nonvanishing eigenvalue λ_1 is not in general available in closed form as it is always rendered as the smallest root of a high-order polynomial equation. Hence, it is difficult to compare λ_1 so determined with experimental observations of the longest relaxation time or the relaxation rate. Fortunately (noting that λ_1 for sufficiently high barriers has exponential dependence on the barrier height), a way of overcoming this difficulty is to utilize [14] the Kramers escape rate theory (for reviews of applications of Kramers’ method, see Refs [2,3,37]).

We saw that Eq. (19) for the Kramers escape rate Γ (reaction velocity for chemical reactions) pertains to a model of a chemical reaction where rare members of an assembly of Brownian particles that are initially trapped in a potential well at A (see Fig. 1) may subsequently under the influence of thermal agitation escape over a high ($\Delta V \gg 1$) barrier at C and descend to the bottom of a very deep potential well B and so never return to A . Thus, we model a chemical reaction (ignoring quantum effects) by introducing a reaction coordinate x such that $x = A$ in species A and $x = B$ in species B (the product state). The reaction is modeled by thermally activated diffusion over the boundary C (the transition state) between the two distinct states. The frequency $\omega_A/2\pi$ that is the frequency of oscillation of a particle in the potential well centered on A is called the attempt frequency. The original Arrhenius equation that is obtained when $\mu = 1$ (corresponding to TST) assumes perpetual thermal equilibrium everywhere at temperature T . Thus, no account is taken of nonequilibrium effects due to the leaking of particles over the potential barrier at C . In reality the Maxwell–Boltzmann distribution no longer holds in the vicinity of the transition state C because the fluctuation dissipation theorem describing the coupling of the reacting particles to their surroundings or heat bath is violated by the Arrhenius equation.

We also saw that Kramers [15] overcame this difficulty by writing the diffusion equation (Klein–Kramers equation) in phase space describing the evolution of the phase space distribution function underlying the Langevin equation for a Brownian particle. He then obtained asymptotic solutions (the Kramers escape rate) for the

smallest nonvanishing eigenvalue λ_1 of the Klein–Kramers equation in the limits of very small and intermediate to high dissipative coupling to the bath. These solutions, which are valid for high barriers ($\Delta V \gg 1$) so that the concept of an escape rate is valid, provide closed form expressions for the reaction rate and its inverse the longest relaxation time $\tau \approx \lambda_1^{-1}$ that may be easily compared with experiment.

We have mentioned that as far as the verification of the turnover formula of Mel’nikov and Meshkov is concerned, few examples of exact calculations based on either the solutions of the Klein–Kramers equation or the numerical simulations of the Brownian dynamics exist. Exceptions include the comparison of the turnover formula with the numerical results for the escape out of a single well, which were given in Refs [46,47] (both based on path integrals) and the study using the matrix continued fraction method of the one-dimensional translational Brownian motion in a potential undertaken by Zhou [48], Ferrando et al. [49–51], Coffey et al. [52,53], and so on. Another exception is the turnover treatment of the same one-dimensional problem and its generalization to diffusion on a surface that was undertaken by Pollak et al. in Refs [54–56] (where a comparison with numerical simulation based on the Langevin equation is again given). Examples of the treatment of rotational Brownian motion problems are even fewer. Coffey et al. [57,58] have considered the one-dimensional rotational Brownian motion of a fixed axis rotator in a potential. Moro and Polimeno [59], Pastor and Szabo [60], and Kalmykov et al. [61,62] tested the Mel’nikov–Meshkov formula for a linear molecule in a uniaxial potential. Furthermore, Kalmykov et al. [63] estimated the reversal time of the magnetization of single-domain ferromagnetic particles possessing nonaxially symmetrical potentials of the magnetocrystalline anisotropy using the results of Coffey et al. [3,64] who extended the depopulation factor calculation to magnetic systems. (We remark that the magnetic relaxation problem differs fundamentally from that of mechanical particles because the undamped equation of motion of the magnetization of a single-domain ferromagnetic particle is the gyromagnetic equation. Thus, the inertia plays no role; the part played by inertia in the mechanical system is essentially mimicked in the magnetic system for nonaxially symmetric potentials by the gyromagnetic term that gives rise to the coupling or “entanglement” of the transverse and longitudinal modes.)

It is the purpose of this section to demonstrate that the Mel’nikov and Meshkov turnover applied to the particular problem of the inertial Brownian motion of a fixed axis rotator in a double-well cosine potential yields an accurate solution for the longest relaxation time λ_1^{-1} for high barriers and for all values of the dissipation. Such a potential allows the flipping of rotators to neighboring wells, thus permitting both relaxation and oscillatory behavior in the same model. The detailed description of the model (in the VHD or noninertial limit) is given in Refs [14,65,66] in connection with site models of dielectric relaxation in molecular crystals and polar liquids. The first attempts to include inertial effects (which are

of importance in the rotation in the VLD region) were made in Refs [67–70]. These calculations are, however, only valid in a restricted range of values of the dissipation parameter and it is only with the advent of the matrix continued fraction method [57,71] that reliable results have become available for all values of the dissipation parameter, including the VLD region [14,16]. Here, we calculate the Kramers escape rate by the Mel’nikov–Meshkov asymptotic (in the sense that it applies for high barriers) and universal (in the sense that it is valid for all values of the damping) turnover formula and compare its inverse with the longest relaxation time predicted by the exact matrix continued fraction solution of the underlying Langevin equation. In the following section, we shall briefly review the derivation of a universal formula for the Kramers escape rate as applied to Brownian rotation in a double-well potential.

Our starting point is the Langevin equation for a dipole μ rotating about a fixed axis [14]

$$I\ddot{\phi}(t) + I\beta\dot{\phi}(t) + \frac{dV}{d\phi}[\phi(t)] = F(t) \quad (134)$$

where I is the moment of inertia of a rotator about the axis of rotation, ϕ is the angle specifying its angular position while $I\beta\dot{\phi}(t)$ and $F(t)$ are the frictional and white noise torques acting on it due to the Brownian motion arising from the heat bath. It is assumed that the random torque $F(t)$ has the white noise properties

$$\overline{F(t)} = 0, \quad \overline{F(t)F(t')} = 2k_B T I \beta \delta(t - t')$$

Here, the overbar denotes the statistical average over a large number of rotators that have at time t identical angular velocity $\dot{\phi}$ and identical angular position ϕ . In accordance with the notation of Refs [14,16], we shall use the notation $\phi(t)$ and $\dot{\phi}(t)$ to denote the random variables while we shall denote their sharp (definite) values or realizations at time t by ϕ and $\dot{\phi}$. The internal field due to molecular interactions is represented by the twofold cosine potential (see Fig. 4)

$$V(\phi) = V_0[\cos(2\phi) - 1] = -2k_B T \sigma \sin^2 \phi \quad (135)$$

where $2\sigma = 2V_0/k_B T$ is the barrier height parameter. The corresponding Klein–Kramers (Fokker–Planck) equation for the joint PDF $W(\phi, \dot{\phi}, t)$ of the angle ϕ and angular velocity $\dot{\phi}$ can be written as [14]

$$\frac{\partial W}{\partial t} = L_{\text{FP}} W \quad (136)$$

where the Fokker–Planck operator L_{FP} is given by [70]

$$L_{\text{FP}} W = -\dot{\phi} \frac{\partial W}{\partial \phi} + \frac{1}{I} \frac{dV}{d\phi} \frac{\partial W}{\partial \dot{\phi}} + \beta \left(\frac{\partial}{\partial \dot{\phi}} (\dot{\phi} W) + \frac{k_B T}{I} \frac{\partial^2 W}{\partial \dot{\phi}^2} \right) \quad (137)$$

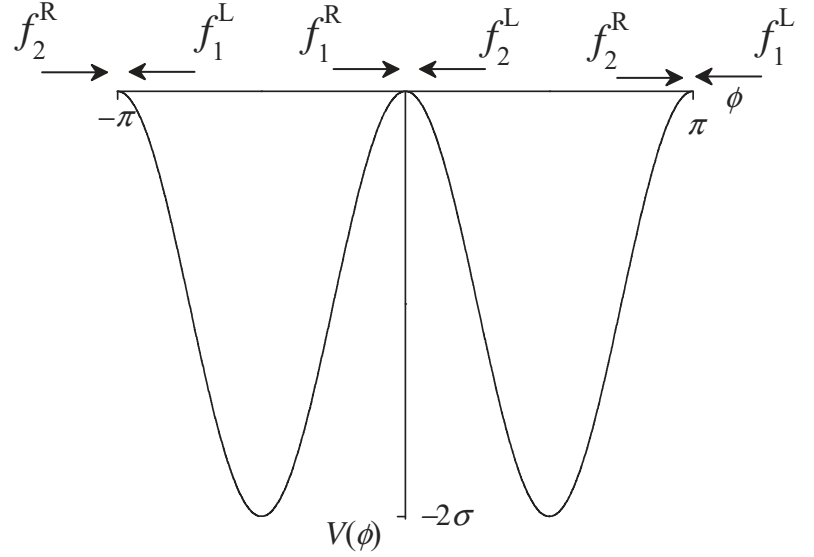


Figure 4. Potential function $V(\phi)$ from Eq. (135).

The first two terms on the right-hand side of Eq. (137) comprise the convective or Liouville term describing in the absence of dissipation the undamped streaming motion along the energy trajectories in phase space corresponding to Hamilton's equations. The last term (the diffusion term) represents the interchange of energy (dissipative coupling) with the heat bath.

Since escape over the potential barrier generated by Eq. (135) is exponentially slow for $\sigma \gg 1$ (high barriers), we may consider the quasistationary distribution $W(\phi, \dot{\phi})$ that does not depend explicitly on the time. Thus, Eq. (136) can be rewritten as $L_{\text{FP}}W = 0$ or

$$I\dot{\phi}\frac{\partial W}{\partial \phi} = \frac{dV}{d\phi}\frac{\partial W}{\partial \dot{\phi}} + I\beta\left(\frac{\partial}{\partial \dot{\phi}}(\dot{\phi}W) + \frac{k_{\text{B}}T}{I}\frac{\partial^2 W}{\partial \dot{\phi}^2}\right) \quad (138)$$

We shall now apply the Mel'nikov–Meshkov method to the potential given by Eq. (135). Since our problem differs in detail from the translational Brownian motion considered by them, we shall give a condensed version of the modifications required in order to apply their method to the present problem. First, we note that the particular Fokker–Planck equation given above may be represented in terms of angle–energy (fast and slow variable) coordinates $\{\phi, E\}$ [where $E = I\dot{\phi}^2/2 + V(\phi)$] using the transformations [57]

$$\frac{\partial}{\partial \dot{\phi}}f^{\text{R,L}}(\phi, p) = \pm\sqrt{2I[E - V(\phi)]}\frac{\partial}{\partial E}f^{\text{R,L}}(\phi, E) \quad (139)$$

$$\frac{\partial}{\partial \phi}f^{\text{R,L}}(\phi, p) = \frac{\partial}{\partial \phi}f^{\text{R,L}}(\phi, E) + \frac{dV(\phi)}{d\phi}\frac{\partial}{\partial E}f^{\text{R,L}}(\phi, E) \quad (140)$$

where

$$f^{\text{R}}(\phi, E) = W(\phi, \dot{\phi}) = W(\phi, \sqrt{2[E - V(\phi)]/I}) \quad (141)$$

$$f^{\text{L}}(\phi, E) = W(\phi, -\dot{\phi}) = W(\phi, -\sqrt{2[E - V(\phi)]/I}) \quad (142)$$

The function f^{R} gives the distribution of rotators rotating clockwise while the function f^{L} gives the distribution of rotators rotating anticlockwise. Thus, we have from Eqs. (138)–(142)

$$\frac{\partial f^{\text{R,L}}}{\partial \phi} = \pm \sqrt{2I[E - V(\phi)]} \beta \frac{\partial}{\partial E} \left[f^{\text{R,L}} + k_{\text{B}} T \frac{\partial}{\partial E} f^{\text{R,L}} \right] \quad (143)$$

Furthermore, if we define the action $s(\phi)$ in the usual way as [2]

$$\frac{ds}{d\phi} = \pm \sqrt{2I[E - V(\phi)]} \quad (144)$$

Equation (143) can compactly be rewritten as the energy–action diffusion equation [3,57]

$$\frac{\partial f^{\text{R,L}}}{\partial s} = \beta \frac{\partial}{\partial E} \left[f^{\text{R,L}} + k_{\text{B}} T \frac{\partial}{\partial E} f^{\text{R,L}} \right] \quad (145)$$

We emphasize that the solution of Eq. (145) will effectively represent Maxwell–Boltzmann distributions deep in the wells of the potential given by Eq. (135) and will differ from those distributions only in a relatively narrow region about the top of the barrier. The behavior being analogous to the VLD case; however, the angle (i.e., the fast variable) dependence of the function f given by the left-hand side of Eq. (145) may not now be neglected near the top of the barrier (compare, e.g., pages 538, 539 of Ref. [3]). Equation (145) has a formal solution using the superposition principle as the convolution [3,57]

$$f^{\text{R,L}}(s, E) = \int_E \int_s g^{\text{R,L}}(s - s', E - E') f^{\text{R,L}}(s', E') ds' dE' \quad (146)$$

where the kernel $g(s, E)$ is the Green function given by Eq. (94) and the limits of integration are determined by the boundary conditions for the functions $f^{\text{R}}(s, E)$ and $f^{\text{L}}(s, E)$ [3,57]. We proceed as follows. Near the barrier, the flux of the left-going particles inside the first well arises by reflection from the barrier of the right-going particles with $E < 0$ (recall that $E \simeq 0$ is the barrier energy) and also from the particles that have crossed over the barrier from the second well with $E > 0$

(see Fig. 4). The same conditions hold for the second well yielding the following relationship between $f_{1,2}^R$ and $f_{1,2}^L$ (subscripts 1 and 2 pertain to the wells)

$$\begin{aligned} f_1^L[\phi'(E), E] &= f_1^R[\phi'(E), E] \\ f_2^R[\phi''(E), E] &= f_2^L[\phi''(E), E], \quad (E < 0) \\ f_1^L(0, E) &= f_2^L(0, E) \\ f_1^R(0, E) &= f_2^R(0, E), \quad (E > 0) \end{aligned}$$

where $\phi'(E)$ and $\phi''(E)$ are the roots of the separatrix equations $V_1(\phi') = E$ and $V_2(\phi'') = E$, respectively. Particles with different energies E are always reflected at different angles ϕ . For $E \sim k_B T$ (the order of magnitude of a fluctuation), however, this difference is small compared to the angular size of the potential well. Thus, we may assume that such particles propagate along trajectories very close to the barrier energy trajectory (defined by $V_1 = V_2 = 0$) and so can be described by identical Green functions (94), namely,

$$g_S(E) = g(S, E) = \frac{1}{\sqrt{4\pi k_B T \beta S}} \exp \left[-\frac{(E + \beta S)^2}{4k_B T \beta S} \right] \quad (147)$$

where $S = S_i$ ($i = 1, 2$) and S_i is the action in the i th well given by

$$S_1 = \int_{-\pi}^0 \sqrt{-2IV(\phi)} d\phi = 4\sqrt{Ik_B T \sigma}, \quad S_2 = \int_0^{\pi} \sqrt{-2IV(\phi)} d\phi = 4\sqrt{Ik_B T \sigma} \quad (148)$$

The complete system of integral equations is then

$$f_i^R(E) = \int_{-\infty}^{\infty} [g_S(E - E') f_i^L(E') U(-E') + g_S(E - E') f_j^R(E') U(E')] dE' \quad (149)$$

$$f_i^L(E) = \int_{-\infty}^{\infty} [g_S(E - E') f_i^R(E') U(-E') + g_S(E - E') f_j^L(E') U(E')] dE' \quad (150)$$

($i, j = 1, 2$ and $i \neq j$), where $U(x)$ is the Heaviside unit step function. The system of four integral Eqs. (149) and (150) can be reduced to two namely

$$f_1(E) = \int_{-\infty}^{\infty} [g_S(E - E')f_1(E')U(-E') + g_S(E - E')f_2(E')U(E')] dE' \quad (151)$$

$$f_2(E) = \int_{-\infty}^{\infty} [g_S(E - E')f_2(E')U(-E') + g_S(E - E')f_1(E')U(E')] dE' \quad (152)$$

where $f_1(E) = f_1^L(E) + f_1^R(E)$ and $f_2(E) = f_2^L(E) + f_2^R(E)$. Equations (151) and (152) indicate that two distinct contributions to f_1 and f_2 exist. One contribution is from particles *reflected* from the barrier with distribution $f_1(E)U(-E)$ and $f_2(E)U(-E)$ and the other is from particles that have *crossed* the barrier with distributions $f_2(E)U(E)$ and $f_1(E)U(E)$.

Now, the escape rate Γ_1 from the well 1 is (see Fig. 4)

$$\Gamma_1 = \int_0^{\infty} [f_1^L(E) + f_1^R(E) - f_2^L(E) - f_2^R(E)] dE = \int_0^{\infty} [f_1(E) - f_2(E)] dE \quad (153)$$

Due to the equivalence of the wells 1 and 2, the escape rate Γ_2 from the well 2 is equal to Γ_1 . These escape rates are related to the lifetime τ of a particle by

$$\tau^{-1} = \Gamma_1 + \Gamma_2 = 2\Gamma_1 = 2 \int_0^{\infty} [f_1(E) - f_2(E)] dE \quad (154)$$

Solving Eqs. (149) and (151) by the Wiener–Hopf method [57], as shown in Appendix A, and using the solution so obtained to evaluate τ^{-1} from Eq. (154), we have

$$\begin{aligned} \tau^{-1} = & \frac{A^2(\Delta)}{\pi\eta A(2\Delta)} \left[\sqrt{\frac{\beta'^2}{4} + \frac{\eta^2}{I} |V''(0)|} - \frac{\beta'}{2} \right] \left[\sqrt{\frac{V''(\phi_1)}{|V''(0)|}} e^{V(\phi_1)/(k_B T)} \right. \\ & \left. + \sqrt{\frac{V''(\phi_2)}{|V''(0)|}} e^{V(\phi_2)/(k_B T)} \right] \end{aligned} \quad (155)$$

where $\eta = \sqrt{I/2k_B T}$ is a characteristic time of the inertial motion, $\beta' = \beta\eta$ is the dimensionless damping parameter,

$$V(\phi_i)/(k_B T) = -2\sigma, \quad |V''(\phi_i)|/I = |V''(0)|/I = 2\sigma/\eta^2$$

$\phi_i = \phi_{\min_i}$ ($i = 1, 2$) are the potential minima in the i th well and $A(\Delta)$ is the depopulation factor defined by Eq. (24) with

$$\Delta = \frac{\beta S}{k_B T} = 4\beta' \sqrt{2\sigma} \quad (156)$$

Thus, the longest relaxation time τ can now be compactly represented via the turnover formula

$$\tau = \frac{A(2\Delta)}{A^2(\Delta)} \tau_{\text{IHD}} \quad (157)$$

where

$$\tau_{\text{IHD}} = \frac{\pi\eta}{\sqrt{\beta'^2 + 8\sigma - \beta'}} e^{2\sigma} \quad (158)$$

is the longest relaxation time in the IHD limit. The leading factor on the right-hand side of Eq. (157) is the correction to the IHD result due to Mel'nikov and Meshkov [10]. If $\beta' \rightarrow \infty$, we have from Eqs. (120) and (157) the VHD formula

$$\tau_{\text{VHD}} = \frac{\pi\eta\beta'}{4\sigma} e^{2\sigma} \quad (159)$$

which is the result of Lauritzen and Zwanzig [65,66] (in our notation). In like manner, in the VLD limit, $\beta' \rightarrow 0$, we have

$$\tau_{\text{VLD}} = \frac{\pi\eta}{8\beta'\sigma} e^{2\sigma} \quad (160)$$

Since the potential is symmetrical, the longest relaxation time τ , Eq. (157), can also be used to estimate the correlation time τ_{\parallel} of the equilibrium correlation function $C(t)$ of the longitudinal component of the dipole moment that for the potential given by Eq. (135) is

$$C(t) = \frac{\langle \sin \phi(0) \sin \phi(t) \rangle_0}{\langle \sin^2 \phi(0) \rangle_0} \quad (161)$$

(the angular brackets denote the equilibrium ensemble average). The correlation time τ_{\parallel} is defined as the area under the curve of $C(t)$, namely,

$$\tau_{\parallel} = \int_0^{\infty} C(t) dt \quad (162)$$

The time τ_{\parallel} may equivalently be defined in terms of the eigenvalues (λ_k) of the Fokker–Planck operator L_{FP} from Eq. (137) because $C(t)$ may be formally written as the discrete set of relaxation modes

$$C(t) = \sum_k c_k e^{-\lambda_k t} \quad (163)$$

Thus, from Eqs. (162) and (163)

$$\tau_{\parallel} = \sum_k c_k / \lambda_k \quad (164)$$

where $\sum_k c_k = 1$. The correlation time τ_{\parallel} unlike the escape rate clearly contains contributions from *all* the eigenvalues λ_k . In general, in order to evaluate $C(t)$ and τ_{\parallel} , a knowledge of all the λ_k and c_k is required. However, in the *high-barrier limit* ($\sigma \gg 1$), $\lambda_1 \sim e^{-2\sigma} \ll \lambda_k$ and for *symmetrical* potentials $c_1 \approx 1 \gg c_k (k \neq 1)$ [14,16] so that the approximation $\tau_{\parallel} \approx 1/\lambda_1$ can be used. In other words, the inverse of the smallest nonvanishing eigenvalue, that is, the longest relaxation time closely approximates the correlation time for symmetrical potentials in the low-temperature (high-barrier) limit.

2. Exact Matrix Continued Fraction Solution of the Langevin Equation

In order to calculate τ_{\parallel} , we shall use matrix continued fractions as developed in Ref. [57]. As shown there we can derive from the Langevin equation (134) the following recurrence relation for the correlation functions $c_{n,q}(t)$, namely,

$$\begin{aligned} \eta \dot{c}_{n,q}(t) + n\beta' c_{n,q}(t) + \frac{iq}{2} [c_{n+1,q}(t) + 2nc_{n-1,q}(t)] \\ - in\sigma [c_{n-1,q+2}(t) - c_{n-1,q-2}(t)] = 0 \end{aligned} \quad (165)$$

where

$$c_{n,q}(t) = \langle \sin \phi(0) H_n[\eta \dot{\phi}(t)] e^{-iq\phi(t)} \rangle, \quad (n \geq 0, -\infty < q < \infty) \quad (166)$$

so that $\text{Im}[c_{0,1}(t)]/\text{Im}[c_{0,1}(0)] = C(t)$, and H_n are the Hermite polynomials [72]. By Laplace transformation, we have from Eq. (165)

$$\begin{aligned} [\eta s + n\beta'] \tilde{c}_{n,q}(s) + \frac{iq}{2} [\tilde{c}_{n+1,q}(s) + 2n\tilde{c}_{n-1,q}(s)] \\ - in\sigma [\tilde{c}_{n-1,q+2}(s) - \tilde{c}_{n-1,q-2}(s)] = \eta c_{0,q}(0)\delta_{n0} \end{aligned} \quad (167)$$

because the initial conditions for $c_{n,q}(0)$ are $c_{0,2q}(0) = 0$ and

$$\begin{aligned} c_{0,2q+1}(0) &= \langle \sin \phi e^{-i(2q+1)\phi} \rangle = \frac{\int_0^{2\pi} \sin \phi e^{-i(2q+1)\phi} e^{-\sigma \cos 2\phi} d\phi}{\int_0^{2\pi} e^{-\sigma \cos 2\phi} d\phi} \\ &= i(-1)^{q+1} \frac{I_q(\sigma) + I_{q+1}(\sigma)}{2I_0(\sigma)} \end{aligned}$$

where the I_n are the modified Bessel functions of the first kind of order n [72]; the other $c_{n,q}(0) = 0$ for $n \geq 1$ because $\langle \sin \phi H_n(\dot{\phi}) e^{-iq\phi} \rangle = 0$ for the equilibrium Maxwell–Boltzmann distribution.

In order to solve Eq. (167), we introduce the column vectors

$$\tilde{\mathbf{C}}_1(s) = \begin{pmatrix} \vdots \\ \tilde{c}_{0,-2}(s) \\ \tilde{c}_{0,-1}(s) \\ \tilde{c}_{0,1}(s) \\ \tilde{c}_{0,2}(s) \\ \vdots \end{pmatrix} \quad \text{and} \quad \tilde{\mathbf{C}}_n(s) = \begin{pmatrix} \vdots \\ \tilde{c}_{n-1,-2}(s) \\ \tilde{c}_{n-1,-1}(s) \\ \tilde{c}_{n-1,0}(s) \\ \tilde{c}_{n-1,1}(s) \\ \tilde{c}_{n-1,2}(s) \\ \vdots \end{pmatrix}, \quad (n \geq 2)$$

Now, Eq. (167) can be rearranged as the set of matrix three-term recurrence equations

$$[\eta s + \beta'(n-1)] \tilde{\mathbf{C}}_n(s) - \mathbf{Q}_n^+ \tilde{\mathbf{C}}_{n+1}(s) - \mathbf{Q}_n^- \tilde{\mathbf{C}}_{n-1}(s) = \eta \delta_{n1} \mathbf{C}_1(0), \quad (n \geq 1) \quad (168)$$

where the column vector $\mathbf{C}_1(0)$ and the matrices \mathbf{Q}_n^+ and \mathbf{Q}_n^- are given in Appendix B.1. By invoking the general method for solving the matrix recurrence equation (168) [14], we have the exact solution for the spectrum $\tilde{\mathbf{C}}_1(s)$ as a matrix continued fraction, namely,

$$\tilde{\mathbf{C}}_1(s) = \eta \Delta_1(s) \mathbf{C}_1(0) \quad (169)$$

$\Delta_n(s)$ is defined by the recurrence equation

$$\Delta_n(s) = \{[\eta s + \beta'(n-1)] \mathbf{I} - \mathbf{Q}_n^+ \Delta_{n+1}(s) \mathbf{Q}_{n+1}^-\}^{-1}$$

and \mathbf{I} is the unit matrix. Having determined $\tilde{\mathbf{C}}_1(s)$, we can evaluate

$$\tau_{\parallel} = \tilde{\mathbf{C}}(0) = \frac{\tilde{c}_{0,-1}(0) - \tilde{c}_{0,1}(0)}{c_{0,-1}(0) - c_{0,1}(0)} \quad (170)$$

as well as the spectrum of the longitudinal correlation function $\tilde{\mathbf{C}}(\omega)$

$$\tilde{\mathbf{C}}(\omega) = \frac{\tilde{c}_{0,-1}(i\omega) - \tilde{c}_{0,1}(i\omega)}{c_{0,-1}(0) - c_{0,1}(0)} \quad (171)$$

The matrix continued fraction solution [Eq. (168)] we have obtained is easily computed. As far as practical calculations of the infinite matrix continued fraction are concerned, we approximate it by a matrix continued fraction of finite order (by putting $\Delta_{n+1} = \mathbf{0}$ at some $n = N$). Simultaneously, we confine the dimensions of the infinite matrices \mathbf{Q}_n^- , \mathbf{Q}_n^+ , and \mathbf{I} to a finite value $M \times M$. Both N and M depend on the dimensionless barrier (σ) and damping (β') parameters and must be chosen taking into account the desired degree of accuracy of the calculation. Both N and M increase with decreasing β' and increasing σ . For example, for $\sigma = 6$ (a relatively high barrier = $12 k_B T$), $N = 50$ and $M = 60$ allows us to obtain six significant digits for $\tau/\eta = 8.88490 \times 10^4$ at $\beta' = 1$ (intermediate damping), while $N = 2300$ and $M = 300$ are required to obtain six significant digits for $\tau/\eta = 1.47885 \times 10^6$ at $\beta' = 0.01$ (low damping). For very low damping and low temperatures, however, the method is difficult to apply because the matrices involved become ill conditioned so that numerical inversions are no longer possible. The problem of convergence of matrix continued fractions is discussed in detail by Risken [16].

We remark that for free Brownian rotation of plane rotators ($\sigma = 0$), the exact analytical solution for $\tilde{\mathbf{C}}(\omega)$ may be expressed [73] in terms of the confluent hypergeometric (Kummer's) function $M(a, b, z)$ [72] (in our notation)

$$\tilde{\mathbf{C}}(\omega) = \frac{2\beta'\eta}{1 + i\omega 2\beta'\eta} M[1, 1 + 2\beta'^{-2}(1 + i\omega 2\beta'\eta), 2\beta'^{-2}] \quad (172)$$

In the VLD and VHD limits, the correlation time $\tau_{\parallel} = \tilde{\mathbf{C}}(0)$ from Eq. (172) yields

$$\tau_{\parallel} \rightarrow \eta\sqrt{\pi} \quad \text{and} \quad \tau_{\parallel} \rightarrow 2\eta\beta' \quad (173)$$

respectively. Equations (172) and (173) provide very useful relations for the purpose of testing the results of numerical calculations.

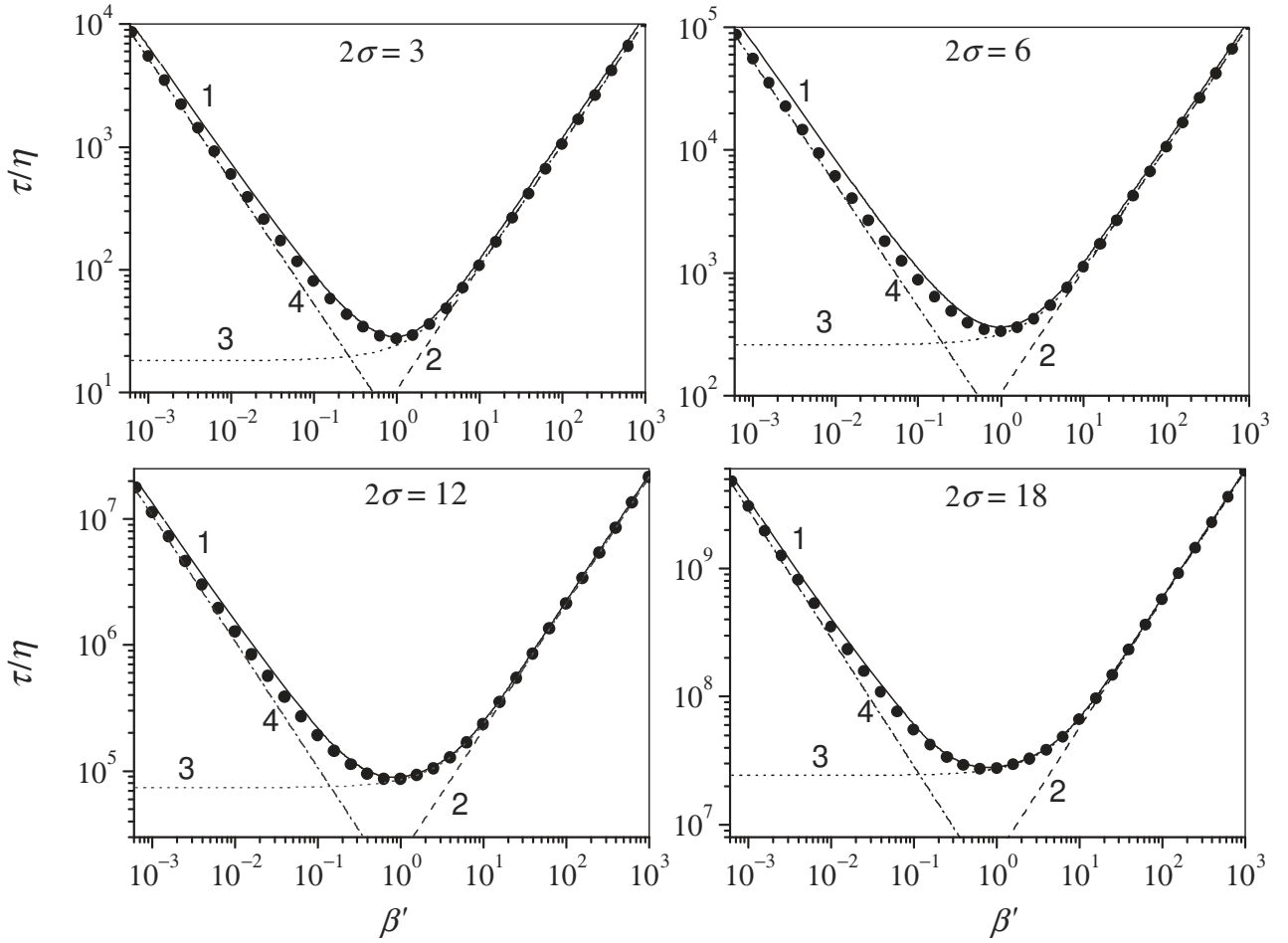


Figure 5. τ/η versus β' for $2\sigma = 3, 6, 12,$ and 18 . Solid lines 1: exact matrix continued fraction solution for the correlation time τ_{\parallel} , Eq. (170); dashed lines 2: the VHD Eq. (159); dotted line 3: the IHD Eq. (158); dashed-dotted lines 4: the VLD Eq. (160); filled circles: the turnover equation (157).

3. Comparison of Exact Matrix Solution with Approximate Analytical Formula

The longest relaxation time τ predicted by the Mel'nikov and Meshkov [10] method, that is, [Eq. (157)] and the correlation time τ_{\parallel} calculated numerically by matrix continued fraction methods from Eqs. (169) and (170) are shown in Figs. 5 and 6 as functions of β' and σ , respectively. Here, the VHD [Eq. (159)], IHD [Eq. (158)], and VLD [Eq. (160)] asymptotes are also shown for comparison. Apparently in the high-barrier limit, Eq. (157) provides a good approximation of the correlation time τ_{\parallel} for all values of the damping parameter β' including the VHD, VLD, and crossover regions.

Furthermore, Eq. (157) yields a reasonable estimate for τ_{\parallel} even for low barriers, $\sigma \sim 1$ (see Fig. 6). However, a marked difference (of the order of 10–40%) between numerical and analytical results exists in the VLD region especially at moderate barriers (this difference decreases with increasing σ and decreasing β' , see Fig. 5). Such behavior occurs for many other systems (see, e.g., Refs [47,50]). Thus in order to improve the accuracy of the turnover formula, Mel'nikov [74] suggested a systematic way of accounting for finite-barrier corrections. Analysis

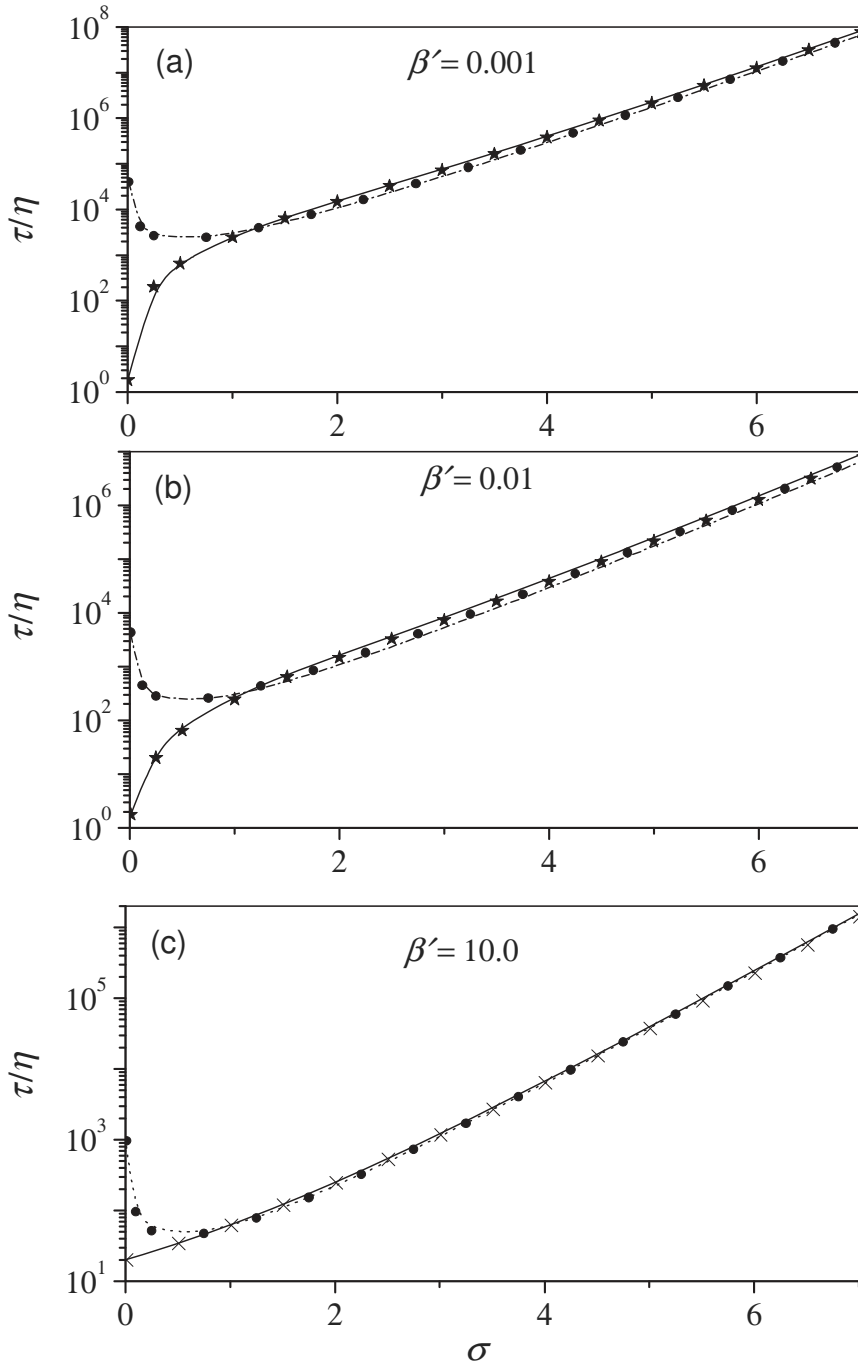


Figure 6. τ/η versus σ for $\beta' = 0.001$ (a; very low damping), $\beta' = 0.01$ (b) and $\beta' = 10$ (c; high damping). Solid lines: exact matrix continued fraction solution for the correlation time τ_{\parallel} , Eq. (170), dashed-dotted lines: the VLD Eq. (160); dashed lines: the VHD Eq. (159) for $\beta' = 10$; filled circles: the turnover equation (157); crosses: the VHD Eq. (176); stars: the VLD Eq. (180).

of the translational Brownian motion in a cosine potential demonstrates that if these are included, the accuracy of the turnover formula is considerably improved [51,75]. His method may also be applied here.

We remark that in principle the accurate calculation of τ_{\parallel} is a much more complicated problem than the evaluation of the smallest nonvanishing eigenvalue alone since all the other eigenvalues give a contribution to τ_{\parallel} (see Eq. (164)). Fortunately, for the problem at hand, an accurate method of estimating τ_{\parallel} in the VHD and VLD limits exists. This method based on a one-dimensional Fokker–Planck equation was first suggested by Szabo [76] in the context of the theory of polarized fluorescent emission in uniaxial liquid crystals. However, it may be used for all other systems with dynamics governed by single variable Fokker–Planck equations.

Namely, one may calculate in intergral form the correlation time τ_A of a dynamic variable $A(x)$ defined as the area under the curve of the normalized autocorrelation function $C_A(t) = \langle A[x(0)] A[x(t)] \rangle_0$. Here, $\langle \rangle_0$ designates the statistical averages over the stationary (equilibrium) distribution function $W_{\text{st}}[x(0)]$ with $x(0)$ defined in the range $x_1 \leq x(0) \leq x_2$ and it is assumed that $\langle A \rangle_0 = 0$. The pertinent feature of these is that an *exact* formula for τ_A , may be expressed in terms of the diffusion coefficient $D^{(2)}(x)$ and $W_{\text{st}}(x)$ only (see, e.g., Ref. [14], Chapter 2, Sections 2.10, and 16, S.9, for details), namely,

$$\tau_A = \frac{1}{\langle A^2 \rangle_0} \int_{x_1}^{x_2} \frac{1}{W_{\text{st}}(x) D^{(2)}(x)} \left[\int_{x_1}^x A(z) W_{\text{st}}(z) dz \right]^2 dx \quad (174)$$

The merit of Eq. (174) is that it yields VHD and VLD asymptotes, valid for *all barrier heights* including *very low* barriers, where the Mel'nikov–Meshkov method is not applicable.

Since the dynamics of the system of planar rotators in the VHD and VLD limits are governed by a single variable, we can obtain accurate VHD and VLD asymptotes by applying Eq. (174). In the high damping limit ($\beta' \gg 1$), the appropriate single variable Fokker–Planck (Smoluchowski) equation for the PDF $W(\phi, t)$ of the orientations of rotators is [14,65]

$$\frac{\partial W}{\partial t} = \frac{1}{2\beta'\eta} \frac{\partial}{\partial \phi} \left(\frac{\partial}{\partial \phi} - 2\sigma \sin 2\phi \right) W \quad (175)$$

Because $D^{(2)}(\phi) = 1/(2\beta'\eta)$ and $A = \sin \phi$, the correlation time τ_{\parallel} of the longitudinal dipole moment autocorrelation function $C(t) = \langle \sin \phi(0) \sin \phi(t) \rangle_0$ is then given by

$$\begin{aligned} \tau_{\parallel} \sim \tau_{\parallel}^{\text{VHD}} &= \frac{2\beta'\eta}{\langle \sin^2 \phi \rangle_0} \int_{-\pi}^{\pi} \frac{1}{W_{\text{st}}(\phi)} \left(\int_0^{\phi} \sin x W_{\text{st}}(x) dx \right)^2 d\phi \\ &= \frac{\beta' \eta e^{2\sigma}}{\sigma [I_1(\sigma) + I_0(\sigma)]} \int_0^{\pi/2} e^{\sigma \cos 2\phi} \text{erf}^2(\sqrt{2\sigma} \cos \phi) d\phi \end{aligned} \quad (176)$$

Here, $W_{\text{st}}(\phi) = e^{-\sigma + 2\sigma \sin^2 \phi} / [2\pi I_0(\sigma)]$ is the equilibrium Boltzmann distribution function [which is a stationary solution of Eq. (175)], $\text{erf}(z)$ is the error function [72], and

$$\langle \sin^2 \phi \rangle_0 = \frac{I_0(\sigma) + I_1(\sigma)}{2I_0(\sigma)} \quad (177)$$

In the opposite low damping limit ($\beta' \ll 1$), one may in order to obtain a single variable Fokker–Planck equation introduce the energy of the dipole

$$\varepsilon = \eta^2 \dot{\phi}^2 - 2\sigma \sin^2 \phi \quad (178)$$

and the time w (phase) measured along a closed trajectory in phase space as action–angle variables [69]. The energy ε varies very slowly with time. Consequently, it is a slow variable in comparison to the phase w . By averaging the Fokker–Planck equation (136) over the fast phase variable w , Praestgaard and van Kampen [69] derived a single variable Fokker–Planck equation for the PDF $W(\varepsilon, t)$ in energy space (in our notation)

$$\frac{\partial}{\partial t} W = \frac{2\beta'}{\eta} \left[\frac{\partial}{\partial \varepsilon} \left(\eta^2 \overline{\dot{\phi}^2}(\varepsilon) - \frac{1}{2} \right) + \eta^2 \frac{\partial^2}{\partial \varepsilon^2} \overline{\dot{\phi}^2}(\varepsilon) \right] W \quad (179)$$

where the double overbar denotes averaging over the fast phase variable. Since

$$D^{(2)}(\varepsilon) = 2\beta' \eta \overline{\dot{\phi}^2}(\varepsilon) = \frac{2\beta'}{\eta} \left(\varepsilon + 2\sigma \overline{\sin^2 \phi}(\varepsilon) \right)$$

the correlation time τ_{\parallel} is then given by [57]

$$\begin{aligned} \tau_{\parallel} \sim \tau_{\parallel}^{\text{VLD}} &= \frac{\eta}{2\beta' \langle \sin^2 \phi \rangle_0} \int_{-2\sigma}^{\infty} \frac{1}{\left[\varepsilon + 2\sigma \overline{\sin^2 \phi}(\varepsilon) \right] W_{\text{st}}(\varepsilon)} \\ &\quad \left[\int_{-2\sigma}^{\varepsilon} \overline{\sin^2 \phi}(x) W_{\text{st}}(x) dx \right]^2 d\varepsilon + \eta\sqrt{\pi} \\ &\approx \frac{\eta\sqrt{\pi}e^{\sigma}}{\beta'\sqrt{2\sigma} [I_0(\sigma) + I_1(\sigma)]} \int_0^1 \frac{[\cosh(2\sigma m) - 1] dm}{(m-1)K(m) + E(m)} + \eta\sqrt{\pi} \quad (180) \end{aligned}$$

where $K(m)$ and $E(m)$ are complete elliptic integrals of the first and second kind, respectively [77]. The calculation of τ_{\parallel} is described in Appendix C. The term $\eta\sqrt{\pi}$ in Eq. (180) is due to the contribution of the free rotation to the correlation time (it is independent of β' , and may be obtained from the solution of the undamped equation $\dot{W} = 0$, see also Appendix C).

The regions of applicability of the VHD and VLD asymptotes from Eqs. (176) and (180) are the same as for the corresponding Fokker–Planck equations (175) and (179), namely, the VHD and VLD regions, respectively; in practice, Eqs. (176) and (180) may be used for $\beta' > 5$ and $\beta' < 0.1$. These VHD and VLD asymptotes are shown in Fig. 6. Apparently they yield a much better estimate for the correlation time than those provided by the turnover formula (the maximum

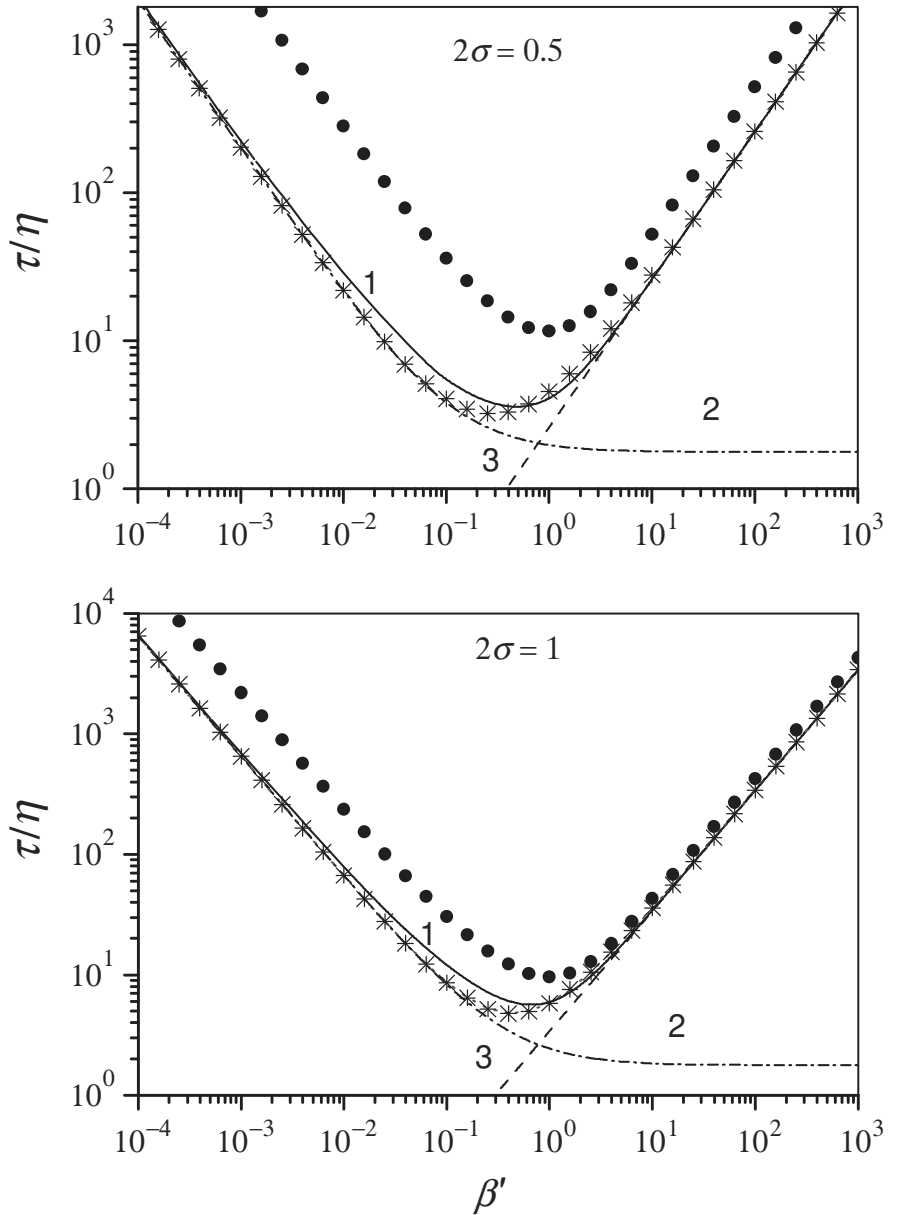


Figure 7. τ/η versus β' for small barrier heights $2\sigma=0.5$ and 1 . Solid lines 1: exact matrix continued fraction solution for τ_{\parallel} , Eq. (170), dashed-dotted lines 2: the VLD Eq. (180); dashed lines 3: the VHD Eq. (176); filled circles: the Mel'nikov–Meshkov equation (157); stars: Eq. (181).

relative deviation between the corresponding curves is less than 25% in the worst cases, usually at the limits of applicability $\beta' \sim 5$ [for Eq. (176)] and $\beta' \sim 0.1$ [for Eq. (180); that is shown in Fig. 6]). In Fig. 7, we compare (176) and (180) with the exact numerical solution for the correlation time at small barriers, where the Mel'nikov–Meshkov turnover formula is not applicable. Here, the simple *ad hoc* extrapolating equation [2]

$$\tau_{\parallel} \sim \tau_{\parallel}^{\text{VLD}} + \tau_{\parallel}^{\text{VHD}} \quad (181)$$

provides a satisfactory estimate of τ_{\parallel} for all damping. We emphasize that Eqs. (176), (180) and (181) can be used for *all barrier heights* σ (see Figs. 6 and 7).

As we shall see later Mel'nikov [8,9] and Pollak et al. [54,78] have also extended the depopulation factor concept to take into account quantum effects. They attempt to generalize the classical formulas given by Kramers for the various escape rate regimes and the depopulation factor by incorporating in their integral equation for

the energy distribution function the quantum reflection factor for a parabolic barrier. We remark that the subject of tunneling in the context of the Kramers escape rate for rotational diffusion problems is of particular relevance in superparamagnetism [14]. Here, the Kramers theory as adapted to nonseparable Hamiltonians has been extensively used [14] to study the reversal of the magnetization in single-domain ferromagnetic particles. Here, the magnetization may be considered as a *macroscopic* object since 10^4 – 10^5 spins are collectively involved. A very important question first posed by Bean and Livingston [79] is Does reversal of magnetization by tunneling occur in such particles? If this reversal mechanism occurs then one would have an important example of *macroscopic quantum tunneling*. It follows, therefore, that the development of an accurate analytical formula for the Kramers escape rate incorporating tunneling effects is vital for the study of magnetization reversal mechanisms in superparamagnets and the possible existence of the macroscopic tunneling phenomenon in such systems. Here, the calculations of Mel'nikov and Meshkov [8,10] may be confirmed as an accurate approximation to the exact escape rate because of the existence of the Klein–Kramers equation describing the evolution of the distribution function in phase space. For single-domain ferromagnetic particles, the corresponding evolution equation is Brown's Fokker–Planck equation for the distribution of the orientations of the magnetic moments on the unit sphere. Thus, in order to verify formulas for the Kramers escape rate that incorporate tunneling effects, it is necessary to define the quantum mechanical master equation that underlies the relaxation process and to solve it numerically. This is accomplished using the Wigner representation of the quantum mechanical master equation [22,80–82] that in the classical limit goes over into the Klein–Kramers equation or Brown's Fokker–Planck equation that we shall discuss in later sections. Such a representation of the quantum mechanical problem as we shall presently see lends itself to solution by the continued fraction method we have described.

E. Escape Rate for a Fixed Axis Rotator in an Asymmetrical Double-Well Potential

1. The Langevin Equation and Differential–Recurrence Equations for Statistical Moments

The Brownian motion in an *asymmetrical* periodic potential also occurs in many physical problems involving a relaxation process including dielectric relaxation and the dynamic Kerr effect of nematic liquid crystals, magnetic relaxation of single-domain ferromagnetic particles, dynamic response of Josephson tunneling junctions, transport phenomena in semiconductors, and so on [14,16,44].

As before one of the most important characteristics associated with the Brownian motion in any asymmetrical multiwell potential is the dependence of the longest relaxation time and the integral relaxation time on the asymmetry

parameter. Thus taking longitudinal dielectric relaxation in a *symmetrical* double-well potential as an example, the longest relaxation time that is the time required to escape the well or the relaxation time of the longest lived relaxation mode is accurately approximated by the integral relaxation time τ_{\parallel} . The integral relaxation time is the area under the decay curve of the electric polarization following the removal of a steady field and corresponds in linear response to the correlation time of the dipole moment. However, in an *asymmetrical* double-well potential for values of the asymmetry parameter well below that required to destroy the double-well nature of the potential, the integral relaxation time may diverge exponentially from the longest relaxation time with consequent suppression of the overbarrier relaxation mode. Thus, the low-frequency dielectric loss associated with this mode effectively disappears. This phenomenon of course does not occur in symmetrical potentials. Hence, it is of some importance to establish the effect of the asymmetry parameter on the relaxation behavior. The dynamical behavior as a function of that parameter has been studied both numerically and analytically when the inertia of a dipole is ignored [83,84]. However, no calculations have been carried out for asymmetrical potentials when inertial effects are included so that the very high-frequency modes associated with the librational motion in the wells of the potential have been excluded.

The longest relaxation time is again essentially the inverse of the smallest non-vanishing eigenvalue λ_1 of the characteristic equation or secular determinant of the relevant dynamical system. However, the longest relaxation time may also be obtained by calculating the mean first passage times (MFPTs) from each of the wells of the potential [85]. As far as λ_1 is concerned, the secular equation may be generated by averaging the appropriate Langevin equation over its realizations in phase space yielding the hierarchy of differential–recurrence equations governing the decay functions of the system. Alternatively, one may expand the solution of the associated probability density diffusion equation (usually the specialized form of the Fokker–Planck equation applicable to separable and additive Hamiltonians comprising the sum of the potential and kinetic energies known as the Klein–Kramers equation) in Fourier series in the position and velocity variables [14,16]. In each of the two methods, the secular determinant results from truncation of the set of differential–recurrence relations at a number large enough to achieve convergence of the resulting set of simultaneous ordinary differential equations. Alternatively, if the problem is represented in the frequency domain so that the more powerful continued fraction method may be used (more powerful in the sense that it is very effective from a computational point of view), many convergents must be taken [16,45]. Thus, λ_1 is not in general available in closed form as it is always rendered as the smallest root of a high-order polynomial equation. Hence, it is difficult to compare λ_1 so determined with experimental observations of the longest relaxation time or the relaxation rate. Fortunately (noting that λ_1 for sufficiently high barriers has exponential dependence on the barrier height),

we again can use the Kramers method [15] in connection with thermally activated escape of particles out of a potential well and also the turnover formula.

Now we saw that most published results have been obtained for potentials with *equivalent* wells. There the symmetry of the potential masks interesting effects, for example, the exponential divergence of the integral relaxation time and the longest relaxation time that may appear for potentials with *nonequivalent* wells so that the asymmetry of the potential can radically alter the characteristics of the relaxation process [14]. Exact numerical and accurate analytical solutions of this problem have been obtained in the very high damping limit when the inertial effects associated with the relaxing population at short times may be ignored. However, it appears that solutions valid for all values of the damping for an asymmetrical potential have not yet been obtained. Here, we demonstrate that the turnover formula when applied to the inertial Brownian motion of a fixed axis rotator in a asymmetrical double-well potential yields an accurate solution for the longest relaxation time λ_1^{-1} for high barriers and for all values of the dissipation. Such a potential allows the flipping of rotators to neighboring wells, thus permitting both relaxation and oscillatory behavior in the same model and so may simultaneously explain both the low-frequency relaxation and the far-infrared absorption spectra of dipolar systems [14,70]. Various applications of this model are discussed in detail in Refs [14,70]. The detailed description of the model for a *symmetrical* double-well potential is given in Ref. [57]. Here, we calculate the escape rate by the Mel'nikov–Meshkov asymptotic (in the sense that it applies for high barriers) and universal (in the sense that it is valid for all values of the damping) formula for an asymmetrical potential. Then we compare the inverse escape rate with the longest relaxation time evaluated from the exact matrix continued fraction solution of the appropriate Langevin equation. Applications of the Mel'nikov–Meshkov asymptote to the estimation of the integral relaxation time (in the present context where linear response is assumed, the correlation time) of the longitudinal relaxation function, the complex susceptibility, and so on, are also discussed and exact solutions for the electric susceptibility valid in all frequency ranges are presented. Here essentially three relaxation time processes exist: (i) a slow overbarrier relaxation process with relaxation time given by λ_1^{-1} that gives rise to low-frequency absorption with an Arrhenius-like relaxation time; (ii) relatively fast near degenerate decay modes in the wells of the potential that may be approximated by a single decay mode and give rise in the frequency domain to weak intermediate frequency absorption, and (iii) high-frequency oscillatory modes that produce absorption in the far-infrared band of frequencies and that are ultimately linked to the Kramers concept of oscillations in a potential well before escape. These three relaxation modes are obviously present in asymmetrical potentials also. However, introducing asymmetry will cause (at a certain critical value of the asymmetry parameter) the overbarrier mode to become so weak that it will be almost completely suppressed while both intrawell and oscillatory modes remain.

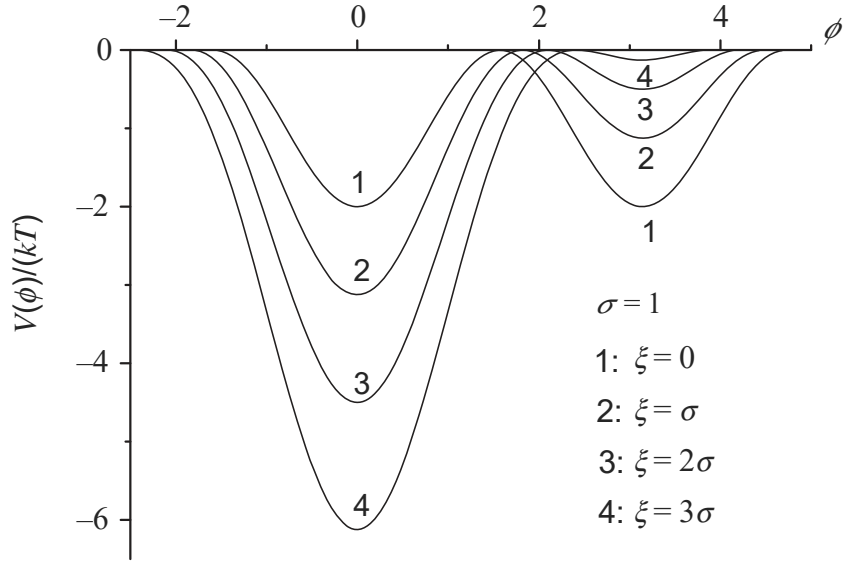


Figure 8. Potential $V(\phi)/(kT) = -2\sigma\cos^2\phi - \xi\cos\phi - \xi^2/(8\sigma)$ for $\sigma=1$ and various values of ξ .

Just as with a symmetrical potential, our starting point is again the Langevin equation (134) for a dipole $\boldsymbol{\mu}$ rotating about an axis normal to the plane of rotation with the only modification that now the internal field due to molecular interactions and the external field are represented by the (periodic) double-well potential (see Fig. 8)

$$V(\phi)/(k_B T) = -2\sigma \cos^2 \phi - \xi \cos \phi - \xi^2/(8\sigma) = -2\sigma(\cos \phi + h)^2 \quad (182)$$

where $\sigma = V_0/(k_B T)$ is the barrier height parameter, $\xi = \mu E/(k_B T)$ is the external field parameter, E is the external field, and $h = \xi/(4\sigma)$. The corresponding Klein–Kramers (Fokker–Planck) equation for the joint distribution function $W(\phi, \dot{\phi}, t)$ is given by Eq. (136).

In orientational relaxation, we see that the quantity of greatest interest is the equilibrium correlation function $C(t)$ of the longitudinal component of the dipole moment defined as

$$C(t) = \frac{\langle \cos \phi(0) \cos \phi(t) \rangle_0 - \langle \cos \phi(0) \rangle_0^2}{\langle \cos^2 \phi(0) \rangle_0 - \langle \cos \phi(0) \rangle_0^2} \quad (183)$$

(the angular brackets denote the equilibrium ensemble average). This allows one to calculate the longitudinal complex susceptibility $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$ defined as [14]

$$\frac{\chi(\omega)}{\chi'(0)} = 1 - i\omega\tilde{C}(\omega) \quad (184)$$

where $\chi'(0) = (\mu^2 N_0/kT) (\langle \cos^2 \phi(0) \rangle_0 - \langle \cos \phi(0) \rangle_0^2)$ is the static susceptibility and N_0 is the number of dipoles per unit volume. Moreover, one can also

calculate the correlation time $\tau_{\parallel} = \tilde{C}(0)$ Eq. (162). As before τ_{\parallel} may equivalently be defined by Eq. (164) in terms of the eigenvalues (λ_k) of the Fokker–Planck operator L_{FP} from Eq. (137). In general, for nonequivalent wells above a critical value of the asymmetry parameter h , τ_{\parallel} may differ exponentially from the inverse of the smallest nonvanishing eigenvalue λ_1^{-1} , which is the longest relaxation time τ of the system [14,83]. In the frequency domain representation of the relaxation process, λ_1 corresponds to the half-width of the spectrum $\tilde{C}(\omega)$ or, equivalently, to the low-frequency maximum of the dielectric loss spectra $\chi''(\omega)$.

First, we briefly present an exact method of solution of the Langevin equation (134) with the potential Eq. (182) based on matrix continued fractions and so an exact evaluation of $\tilde{C}(\omega)$, τ_{\parallel} and λ_1^{-1} . Then we show how, λ_1^{-1} and the low-frequency part of $\tilde{C}(\omega)$ can be evaluated in the low-temperature (high-barrier) limit from the Mel'nikov–Meshkov turnover equation.

Just as with $\xi = 0$, the Langevin equation (134) allows us (details in Ref. [58]) to derive a hierarchy of recurrence equations for the equilibrium correlation functions $c_{n,q}(t)$ defined as

$$c_{n,q}(t) = \langle \cos \phi(0) H_n[\eta \dot{\phi}(t)] e^{-iq\phi(t)} \rangle_0 - \langle \cos \phi(0) \rangle_0 \langle H_n[\eta \dot{\phi}(0)] e^{-iq\phi(0)} \rangle_0 \quad (185)$$

where $\phi(0)$ is the initial value of $\phi(t)$ and $\eta = \sqrt{I/(2k_{\text{B}}T)}$. These differential–recurrence equations for $c_{n,q}(t)$ are given by [58]

$$\begin{aligned} \eta \frac{d}{dt} c_{n,q}(t) = & -n\beta' c_{n,q}(t) - \frac{iq}{2} [c_{n+1,q}(t) + 2nc_{n-1,q}(t)] \\ & - in\sigma [c_{n-1,q+2}(t) - c_{n-1,q-2}(t)] \\ & - 2in\sigma h [c_{n-1,q+1}(t) - c_{n-1,q-1}(t)] \end{aligned} \quad (186)$$

The solution of the recurrence equation (186) can be obtained by a matrix continued fraction method [58]. We remark that exactly the same hierarchy may be obtained by first calculating the Green function of the Fokker–Planck equation (136) and then averaging the hierarchy over the equilibrium Maxwell–Boltzmann distribution.

By Laplace transformation, we have from Eq. (186)

$$\begin{aligned} [\eta s + n\beta'] \tilde{c}_{n,q}(s) = & \eta c_{0,q}(0) \delta_{n0} - \frac{iq}{2} [\tilde{c}_{n+1,q}(s) + 2n\tilde{c}_{n-1,q}(s)] \\ & - in\sigma [\tilde{c}_{n-1,q+2}(s) - \tilde{c}_{n-1,q-2}(s)] \\ & - 2in\sigma h [\tilde{c}_{n-1,q+1}(s) - \tilde{c}_{n-1,q-1}(s)] \end{aligned} \quad (187)$$

Here all other $c_{n,q}(0) = 0$ for $n \geq 1$ because $\langle \cos \phi H_n(\phi) \rangle_0 = 0$ for the equilibrium Maxwell–Boltzmann distribution. In order to solve Eq. (187), we introduce the column vectors

$$\tilde{\mathbf{C}}_1(s) = \begin{pmatrix} \vdots \\ \tilde{c}_{0,-2}(s) \\ \tilde{c}_{0,-1}(s) \\ \tilde{c}_{0,1}(s) \\ \tilde{c}_{0,2}(s) \\ \vdots \end{pmatrix} \quad \text{and} \quad \tilde{\mathbf{C}}_n(s) = \begin{pmatrix} \vdots \\ \tilde{c}_{n-1,-2}(s) \\ \tilde{c}_{n-1,-1}(s) \\ \tilde{c}_{n-1,0}(s) \\ \tilde{c}_{n-1,1}(s) \\ \tilde{c}_{n-1,2}(s) \\ \vdots \end{pmatrix}, \quad (n \geq 2)$$

Now, Eq. (187) can be rearranged as the set of matrix three-term recurrence equations

$$[\eta s + \beta'(n-1)] \tilde{\mathbf{C}}_n(s) - \mathbf{Q}_n^+ \tilde{\mathbf{C}}_{n+1}(s) - \mathbf{Q}_n^- \tilde{\mathbf{C}}_{n-1}(s) = \eta \delta_{n1} \mathbf{C}_1(0) \quad (188)$$

where the column vector $\mathbf{C}_1(0)$ and the matrices \mathbf{Q}_n^+ and \mathbf{Q}_n^- are given in Appendix B. By invoking the general method for solving the matrix recurrence Eq. (188) [14], we have the exact solution for the spectrum $\tilde{\mathbf{C}}_1(s)$ in terms of a matrix continued fraction, namely [58]

$$\tilde{\mathbf{C}}_1(s) = \eta \mathbf{\Delta}_1(s) \mathbf{C}_1(0) \quad (189)$$

where $\mathbf{\Delta}_n(s)$ is defined by the recurrence equation

$$\mathbf{\Delta}_n(s) = \{ [\eta s + \beta'(n-1)] \mathbf{I} - \mathbf{Q}_n^+ \mathbf{\Delta}_{n+1}(s) \mathbf{Q}_{n+1}^- \}^{-1}$$

and \mathbf{I} is the unit matrix.

Having determined $\tilde{\mathbf{C}}_1(s)$, we can evaluate the spectrum

$$\tilde{C}(\omega) = \frac{\tilde{c}_{0,-1}(i\omega) + \tilde{c}_{0,1}(i\omega)}{c_{0,-1}(0) + c_{0,1}(0)} \quad (190)$$

of the equilibrium correlation function $C(t)$, the longitudinal complex susceptibility $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$ and the correlation time τ_{\parallel} . By using matrix continued fractions, one can also estimate the smallest nonvanishing eigenvalue λ_1 of the Fokker–Planck operator [that is λ_1 of the hierarchy of Eq. (186)], Eq. (137), from the secular equation [14,16]

$$\det[\lambda_1 \tau_N \mathbf{I} + \mathbf{Q}_1 + \mathbf{Q}_1^+ \mathbf{\Delta}_2(-\lambda_1) \mathbf{Q}_2^-] = 0 \quad (191)$$

We remark that λ_1 can also be evaluated from the half-width of the spectrum $\tilde{C}(\omega)$ or, equivalently, from the low-frequency maximum of the dielectric loss spectra $\chi''(\omega)$. By utilizing general properties of Fourier transforms, we may also obtain simple asymptotic equations for $\chi(\omega)$ in the low- and high-frequency limits. We have

$$\frac{\chi''(\omega)}{\chi'(0)} = \omega \int_0^{\infty} C(t) dt + \dots = \omega\tau_{\parallel} \quad (192)$$

for $\omega \rightarrow 0$, and

$$\frac{\chi''(\omega)}{\chi'(0)} \sim -\frac{\dot{C}(0)}{\omega} + \frac{\ddot{C}(0)}{\omega^3} + \dots \quad (193)$$

for $\omega \rightarrow \infty$. Here $\dot{C}(0) = 0$ and

$$\ddot{C}(0) = \frac{\ddot{c}_{0,-1}(0) + \ddot{c}_{0,1}(0)}{c_{0,-1}(0) + c_{0,1}(0)} = \frac{\beta'}{2\eta^3} \left[1 - \sigma + 2\sigma h \frac{c_{0,2}(0)}{c_{0,1}(0)} + \sigma \frac{c_{0,3}(0)}{c_{0,1}(0)} \right] \quad (194)$$

We remark that for free Brownian rotation of planar rotators ($\sigma = 0$ and $h = 0$), λ_1 becomes in the VLD and VHD limits

$$\lambda_1 \rightarrow 1/\eta\sqrt{\pi} \quad \text{and} \quad \lambda_1 \rightarrow 1/2\eta\beta' \quad (195)$$

respectively. Equation (195) provides bounds for the purpose of testing the results of numerical calculations. Moreover, for $\sigma = 0$ and $h = 0$, the calculation shows that the matrix continued fraction algorithm yields the same numerical results for $\tilde{C}(\omega)$ as the exact analytical solution, Eq. (172), for the free rotational diffusion.

2. Turnover Formula for λ_1

By solving the Fokker–Planck equation, converted to an energy–action diffusion equation, by the Wiener–Hopf method, Mel'nikov and Meshkov have evaluated the inverse of the longest relaxation time $\tau^{-1} = \lambda_1$ for the translational motion of a Brownian particle of mass M in a double-well potential $V(x)$ with nonequivalent wells as [10]

$$\tau = \frac{A[\beta(S_1 + S_2)/k_B T]}{A(\beta S_1/k_B T)A(\beta S_2/k_B T)} \tau_{\text{IHD}} \quad (196)$$

Here, τ_{IHD} is the longest relaxation time in the IHD limit that can be estimated as

$$\tau_{\text{IHD}}^{-1} = \Gamma_1^{\text{IHD}} + \Gamma_2^{\text{IHD}} \quad (197)$$

where Γ_1^{IHD} and Γ_2^{IHD} are the Kramers IHD escape rates from the wells 1 and 2, respectively, β is a damping coefficient for rotational motion, S_1 and S_2 are the corresponding action variables, and $A(\Delta)$ is given by Eq. (24). The leading factor on the right-hand side of Eq. (196) is the correction to the IHD escape rate due to Mel'nikov and Meshkov (the depopulation factor). The escape rates Γ_1^{IHD} and Γ_2^{IHD} are evaluated from the Kramers IHD formula [15]

$$\Gamma_i \sim \frac{\omega_A^i}{2\pi} \left(\sqrt{1 + \frac{\beta^2}{4\omega_C^i} - \frac{\beta}{2\omega_C^i}} \right) e^{-\Delta V_i/kT}$$

where $\omega_A^i = \sqrt{V''(A_i)/M}$ and $\omega_C^i = \sqrt{|V''(C)|/M}$ are the angular frequencies of oscillation of a particle in the potential well i at minimum C_i and at the barrier coordinate C , the double prime denotes the second derivative with respect to x , and $\Delta V_i = [V(C) - V(A_i)]/(k_B T)$ is the dimensionless potential barrier.

The detailed derivation of the turnover formula for orientational relaxation of a planar rotator in two equivalent wells has been given in the previous section. This derivation is easily generalized to the calculation of the longest relaxation time of the orientational relaxation in the potential with two nonequivalent wells, Eq. (182), yielding the turnover formula, Eq. (196), where τ_{IHD}^{-1} is now given by [58]

$$\begin{aligned} \tau_{\text{IHD}}^{-1} &= \frac{1}{\pi\eta} \left[\sqrt{\frac{\beta'^2}{4} + \frac{\eta^2}{I} |V''(\phi_0)|} - \frac{\beta'}{2} \right] \left[\sqrt{\frac{V''(0)}{|V''(\phi_0)|}} e^{\Delta V_1} + \sqrt{\frac{V''(\pi)}{|V''(\phi_0)|}} e^{\Delta V_2} \right] \\ &= \frac{e^{-2\sigma(1-h)^2}}{2\pi\eta} \left[\sqrt{\beta'^2 + 8\sigma(1-h^2)} - \beta' \right] \left[\frac{1}{\sqrt{1-h}} e^{-8\sigma h} + \frac{1}{\sqrt{1+h}} \right] \end{aligned} \quad (198)$$

$\phi_1 = 0$ and $\phi_2 = \pi$ are the potential minima in wells 1 and 2, $\phi_0 = \pi - \arccos h$ is the barrier coordinate found from the condition $V(\phi_0) = 0$ (see Fig. 8),

$$\Delta V_{1,2} = -2\sigma(1 \pm h)^2, \quad \frac{\eta^2}{I} |V''(\phi_0)| = 2\sigma(1 - h^2)$$

$$\frac{\eta^2}{I} V''(0) = 2\sigma(1 + h), \quad \frac{\eta^2}{I} V''(\pi) = 2\sigma(1 - h)$$

$$\frac{\beta S_1}{k_B T} = \frac{\beta}{k_B T} \int_{-\phi_0}^{\phi_0} \sqrt{-2IV(\phi)} d\phi = 4\beta' \sqrt{2\sigma} (\sqrt{1-h^2} + h\pi - h \arccos h)$$

$$\frac{\beta S_2}{k_B T} = \frac{\beta}{k_B T} \int_{\phi_0}^{2\pi-\phi_0} \sqrt{-2IV(\phi)} d\phi = 4\beta' \sqrt{2\sigma} (\sqrt{1-h^2} - h \arccos h)$$

If $\beta' \rightarrow \infty$, we have from Eqs. (120), (196) and (198) the VHD formula [58]

$$\tau_{\text{VHD}} = \frac{\pi\eta\beta' e^{2\sigma(1-h)^2}}{2\sigma(\sqrt{1-h} + \sqrt{1+h} e^{-8\sigma h})} \quad (199)$$

In like manner, in the VLD limit, $\beta' \rightarrow 0$, we obtain [58]

$$\tau_{\text{VLD}} = \frac{\pi\eta e^{2\sigma(1-h)^2} (\pi h/2 + \sqrt{1-h^2} - h \arccos h)}{4\beta'\sigma (\sqrt{1-h} + \sqrt{1+h} e^{-8\sigma h}) (h\pi + \sqrt{1-h^2} - h \arccos h) (\sqrt{1-h^2} - h \arccos h)} \quad (200)$$

For $h = 0$, the relaxation times from Eqs. (198)–(200) reduce to Eqs. (158)–(160) for equivalent wells [57].

3. The VHD and VLD Asymptotes for τ_{\parallel}

As far as the calculation of the longitudinal correlation time τ_{\parallel} is concerned, we saw that an accurate analytical estimation of τ_{\parallel} from Eq. (162) poses a much more complicated problem than the evaluation of the smallest nonvanishing eigenvalue alone since all the other eigenvalues contribute to τ_{\parallel} . Fortunately, as we saw an estimate τ_{\parallel} in the VHD and VLD limits that can be given using Eq. (174).

As before in the high damping limit ($\beta' \gg 1$), the appropriate single variable Fokker–Planck (Smoluchowski) equation for the PDF $W(\phi, t)$ of the orientations of rotators is [58]

$$\frac{\partial W}{\partial t} = \frac{\sigma}{\beta'\eta} \frac{\partial}{\partial \phi} [(\sin 2\phi + 2h \sin \phi) W] + \frac{1}{2\beta'\eta} \frac{\partial^2 W}{\partial \phi^2} \quad (201)$$

Because the diffusion coefficient $D^{(2)} = (2\beta'\eta)^{-1}$, the correlation time of the longitudinal dipole moment autocorrelation function in the VHD limit is given by [58]

$$\tau_{\parallel} \sim \tau_{\parallel}^{\text{VHD}} = \frac{2\beta'\eta}{\langle \cos^2 \phi \rangle_0 - \langle \cos \phi \rangle_0^2} \int_0^{2\pi} \frac{1}{W_0(\phi)} \left[\int_0^{\phi} (\cos \phi' - \langle \cos \phi' \rangle_0) W_0(\phi') d\phi' \right]^2 d\phi \quad (202)$$

where $W_0(\phi)$ is the equilibrium Boltzmann distribution function given by

$$W_0(\phi) = \int W_0(\dot{\phi}, \phi) d\dot{\phi} = e^{2\sigma \cos^2 \phi + 4\sigma h \cos \phi} / \int_0^{2\pi} e^{2\sigma \cos^2 \phi + 4\sigma h \cos \phi} d\phi \quad (203)$$

[this function is a stationary solution of Eq. (201)]; $\langle \cos^2 \phi \rangle_0$ and $\langle \cos \phi \rangle_0$ can be calculated as described in Appendix B.2.

In the opposite low damping limit ($\beta' \ll 1$), in order to obtain a single variable Fokker–Planck equation, one may introduce as variables the energy of the dipole

$$\varepsilon = \eta^2 \dot{\phi}^2 - 2\sigma \cos^2 \phi - 4\sigma h \cos \phi \quad (204)$$

and the time w (phase) measured along a closed trajectory in phase space as action–angle variables [69]. The energy ε varies very slowly with time. Consequently, it is a slow variable in comparison to the phase w . Now we saw that averaging the Fokker–Planck equation (136) over the fast phase variable w , Praestgaard and van Kampen [69] have derived a single variable Fokker–Planck equation for the PDF $W(\varepsilon, t)$ in energy space (in our notation)

$$\frac{\partial}{\partial t} W = \frac{2\beta'}{\eta} \left[\frac{\partial}{\partial \varepsilon} \left(\eta^2 \overline{\dot{\phi}^2}(\varepsilon) - \frac{1}{2} \right) + \eta^2 \frac{\partial^2}{\partial \varepsilon^2} \overline{\dot{\phi}^2}(\varepsilon) \right] W \quad (205)$$

where the double overbar denotes averaging over the fast phase variable. Because the diffusion coefficient $D^{(2)} = 2\beta' \eta \overline{\dot{\phi}^2}(\varepsilon)$, the correlation time τ_{\parallel} is then given by [58]

$$\tau_{\parallel} \sim \tau_{\parallel}^{\text{VLD}} = \eta \sqrt{\pi} + \tau_+ + \tau_- \quad (206)$$

where

$$\tau_{\pm} = \frac{1}{(\langle \cos^2 \phi \rangle_0 - \langle \cos \phi \rangle_0^2)} \int_{-2\sigma(1\pm 2h)}^{\infty} \left(\int_{-2\sigma(1\pm 2h)}^{\varepsilon} \left(\overline{\cos \phi}(\varepsilon') - \langle \cos \phi \rangle_0 \right) W_0(\varepsilon') d\varepsilon' \right)^2 \times \frac{d\varepsilon}{2\beta' \eta \overline{\dot{\phi}^2}(\varepsilon) W_0(\varepsilon)} \quad (207)$$

and $\eta^2 \overline{\dot{\phi}^2}(\varepsilon) = \varepsilon + 2\sigma \overline{\cos^2 \phi}(\varepsilon) + 4\sigma h \overline{\cos \phi}(\varepsilon)$. The calculation of $W_0(\varepsilon)$, $\overline{\cos^2 \phi}(\varepsilon)$, $\overline{\cos \phi}(\varepsilon)$, and the integrals in Eqs. (207) are described in Appendix C.2. As already mentioned, the term $\eta \sqrt{\pi}$ in Eq. (206) represents the contribution of the free rotation to the correlation time.

The regions of applicability of the asymptotes from Eqs. (202) and (206) are the same as for the corresponding Fokker–Planck equations (201) and (205), namely, the VHD ($\beta' \gg 1$) and VLD ($\beta' \ll 1$) regions, respectively; in practice, Eqs. (202) and (206) may be used for $\beta' > 5$ and $\beta' < 0.1$.

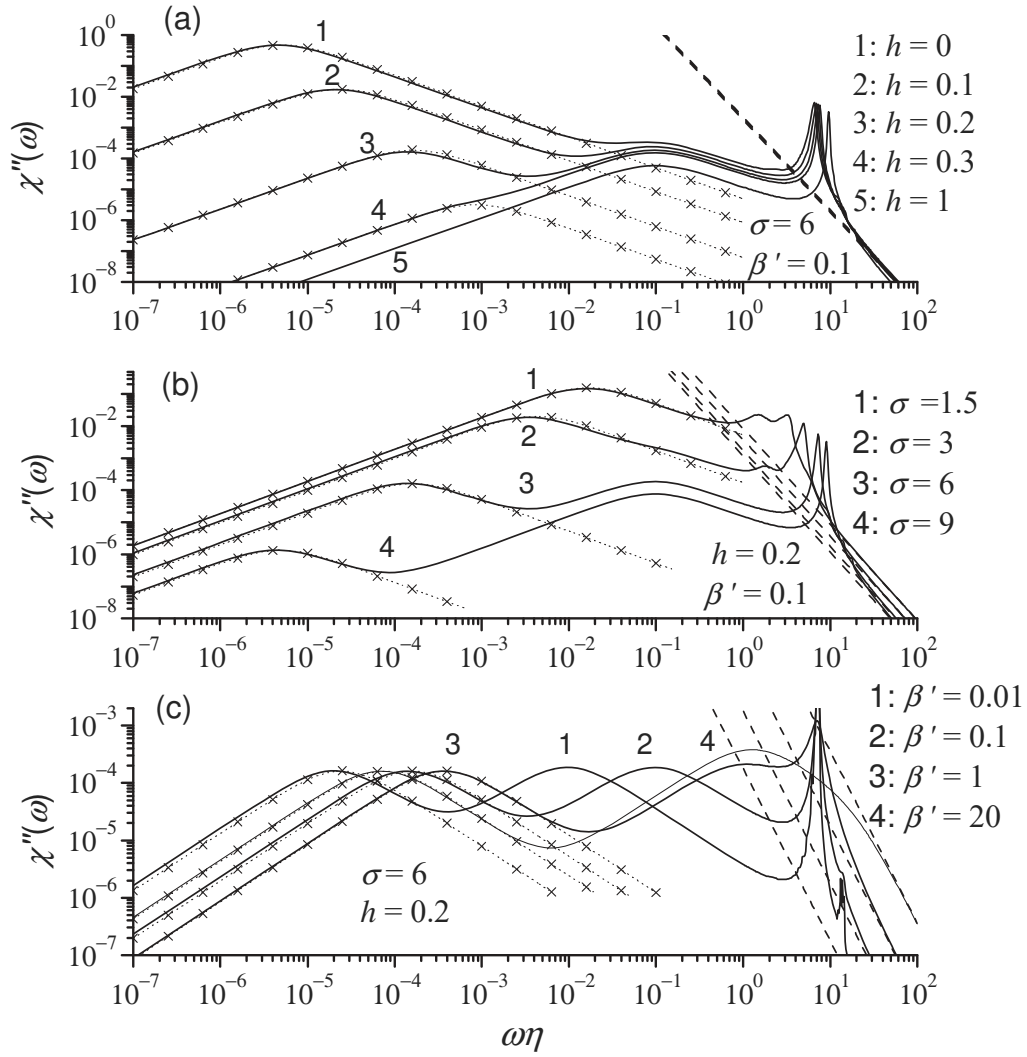


Figure 9. Dielectric loss spectra (solid lines) for various values of σ , β' and h . The Debye spectra [Eq. (208)] are shown by dotted lines with crosses. The high-frequency asymptotes [Eq. (193)] are shown by dashed lines.

4. Comparison of the Exact Matrix Solution with Analytical Approximations

The imaginary $\chi''(\omega)$ part of the complex susceptibility for various values of the anisotropy parameter σ , the asymmetry parameter h , and the friction coefficient β' are shown in Fig. 9 [the calculations were carried out for $\mu^2 N_0 / (k_B T) = 1$]. In general, three bands again appear in the dielectric loss $\chi''(\omega)$ spectra. One relaxation band dominates the low-frequency part of the spectra and is due to the slow overbarrier relaxation of the dipoles in the double-well potential. The characteristic frequency $\omega_R \approx \lambda_1$ of this low-frequency band strongly depends on σ and h as well as on the friction parameter β' . Regarding the barrier height or σ dependence, the frequency ω_R decreases exponentially as σ is raised. This behavior occurs because the probability of escape of a dipole from one well to another over the potential barrier exponentially decreases with increasing σ . As far as the dependence of the low-frequency part of the spectrum for large friction (small inertial effects) $\beta' > 10$ is concerned, the frequency ω_R decreases as β' increases

as is apparent by inspection of curves in Fig. 9c. For small friction (large inertial effects) $\beta' < 0.1$, the frequency ω_R decreases with decreasing β' for given values of σ and h (cf. curves 1–3 in Figs. 9c). This low-frequency part of the spectrum may be approximated by the Debye equation

$$\frac{\chi(\omega)}{\chi'(0)} = \frac{1 - \Delta_1}{1 + i\omega\tau} + \Delta_1 \quad (208)$$

where the longest relaxation time $\tau = 1/\lambda_1$ is given by Eq. (157) and Δ_1 now represents a parameter accounting for the contribution of the high-frequency modes. As h increases, the magnitude of the low-frequency band decreases and this band disappears entirely for $h > 1$ (see Fig. 9a) where the double-well nature of the potential is destroyed.

A very high-frequency band is visible in all the figures due to the fast inertial librations of the dipoles in the potential wells. This band corresponds to the terahertz (far-infrared) range of frequencies and is usually associated with the Poley absorption [86] and again is a manifestation of the Kramers oscillations giving rise *inter alia* to the VLD escape rate. For $\sigma \gg 1$ and $h \approx 0$, the characteristic frequency of librations ω_L increases as $\sim \eta^{-1} \sqrt{\sigma}$. As far as the behavior as a function of β' is concerned, the amplitude of the high-frequency band decreases progressively with increasing β' , as one would intuitively expect. While for small friction (large inertial effects) $\beta' \ll 1$, a fine structure appears in the high-frequency part of the spectra [due to resonances at the fundamental and its higher harmonic frequencies of the almost free motion in the (anharmonic) potential]. We remark that the high-frequency ($\omega \gg \omega_L$) behavior of $\chi''(\omega)$ is entirely determined by the inertia of the system and is described by Eq. (193) (these high-frequency asymptotes are also shown in Fig. 9 for comparison). Again it is apparent that between the low-frequency and very high-frequency bands, a *third* band exists in the dielectric loss spectra. This band is due to the high-frequency relaxation or decay modes of the dipoles in the potential wells, which will always exist in the spectra even in the noninertial limit [14]. Such relaxation modes are generally termed the *intrawell modes*.

Thus, one may conclude that the asymmetrical double-well potential gives rise to three distinct relaxation processes: (i) a slow low-frequency overbarrier mode, (ii) relatively fast intermediate frequency modes due to the near degenerate exponential decays in the wells of the potential, and (iii) fast high-frequency oscillatory (librational) modes in the wells of the potential. If the asymmetry parameter that is strongly dependent on the precise details of the potential [14] is regarded as a structural relaxation parameter in the sense used by Gilroy and Philips [87], it appears that the structural parameter can effectively destroy the low-frequency relaxation mode due to the overbarrier relaxation. Thus, above the critical value of that parameter the system is no longer effectively a multiwell system as the

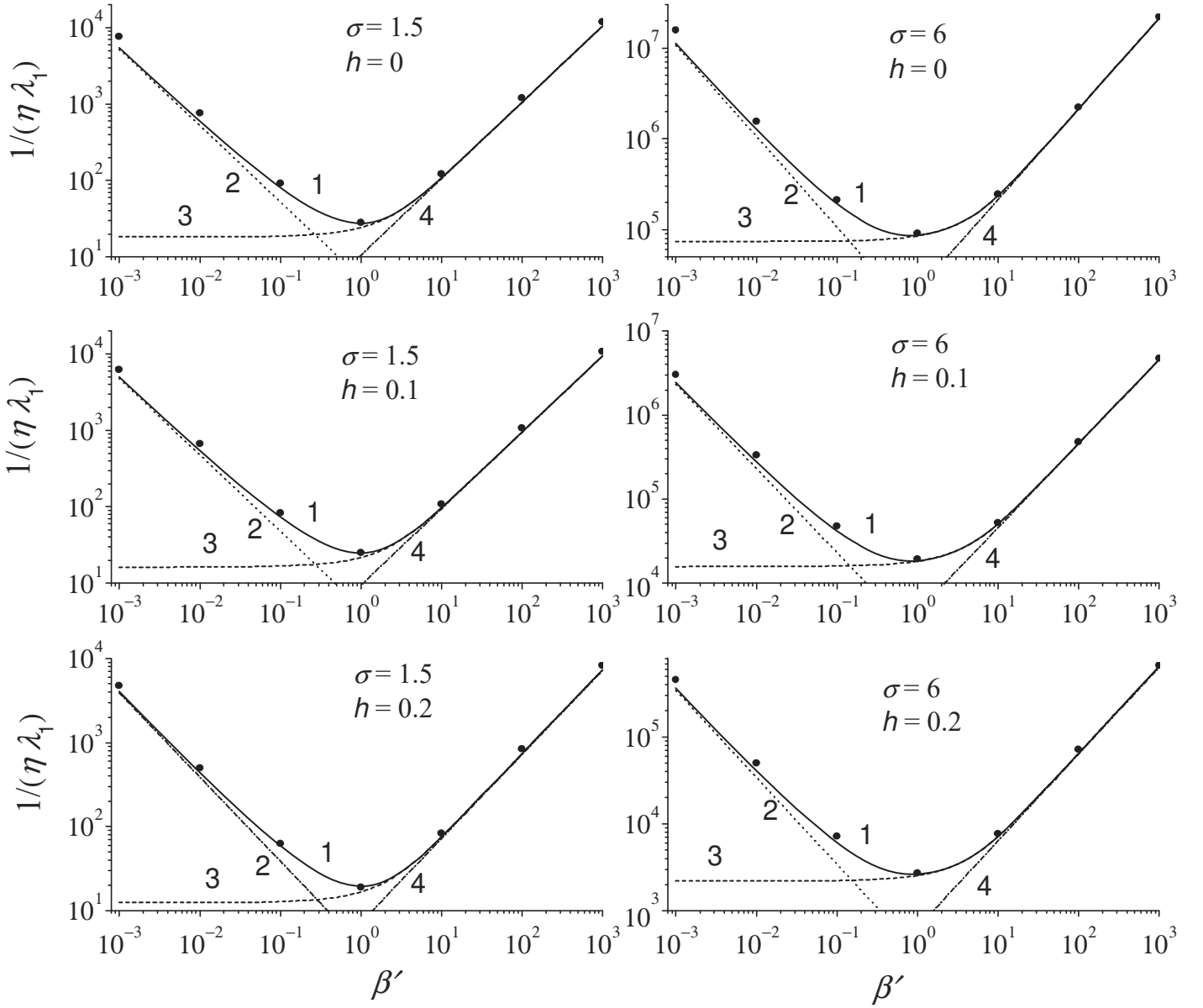


Figure 10. Longest relaxation time $\tau = 1/\lambda_1$ versus β' for $\sigma = 1.5$ and 6 , and $h = 0.0, 0.1,$ and 0.2 . Solid lines 1: the universal equation (196); dashed-dotted lines 4: the VHD Eq. (199); dashed lines line 3: the IHD Eq. (198); dotted 4: the VLD Eq. (200); filled circles: exact matrix continued fraction solution.

population behaves like that of a single-well potential. Hence, we are left with fast near degenerate exponential decays in the well accompanied by high-frequency oscillatory modes arising from inertial effects due to the small oscillations in the well (cf. Fig. 9a).

The longest relaxation time τ predicted by the turnover [10] method [Eq. (196)] and the smallest nonvanishing eigenvalue λ_1 calculated numerically by matrix continued fraction methods as the low-frequency maximum of the dielectric loss spectra $\chi''(\omega)$ are shown in Fig. 10 as functions of β' for various values of h and σ . Here, the VHD [Eq. (199)], IHD [Eq. (198)], and VLD [Eq. (200)] asymptotes are also shown for comparison. Apparently in the high-barrier limit, Eq. (196) provides a good approximation to λ_1 for all β' including the VHD, VLD, and

turnover regions. Furthermore, Eq. (196) yields a reasonable estimate for λ_1 even for $\sigma \approx 1$.

The quantitative agreement in damping behavior may be explained as follows. The escape rate as a function of the barrier height parameter σ for large σ is approximately Arrhenius in character and arises from an *equilibrium* property of the system (namely the Boltzmann distribution at the bottom of the well). On the other hand, the damping dependence of the escape rate is due to *nonequilibrium* (dynamical) properties of the system and so is contained in the prefactor A only, the detailed nature of which depends on the behavior of the energy distribution function at the barrier points [3]. The Mel'nikov–Meshkov approach [8] yields the distribution function at the saddle point for all values of the damping allowing one to evaluate the damping dependence of the prefactor $\mu \sim A$ in Eq. (19). We remark that as emphasized by Kramers, it is hardly ever of any practical importance to improve on the accuracy of the IHD or VLD formulas themselves because in experimental situations where relaxation is studied, one has only estimates of the prefactor within a certain degree of accuracy that is difficult to evaluate. For example, little detailed information about the value of β' exists. Nevertheless, it is important to predict the behavior of the relaxation times and spectra as a function of β' using analytical methods such as the ones used here because of the detailed information they yield about the various mechanisms, for example, overbarrier, intrawell, and resonance modes underlying the relaxation process. The description of the relaxation processes in the context of Eq. (196) neglects quantum effects that are important at very low temperatures and necessitate an appropriate quantum mechanical treatment. Mel'nikov [10] and Rips and Pollak [78] have extended the turnover formula for mechanical particles to account for quantum effects in a semiclassical way (see Section III).

The VHD and VLD asymptotes for τ_{\parallel} are shown in Figs. 11 and 12. In Fig. 11, we compare Eqs. (202) and (206) with the exact numerical solution for the correlation time τ_{\parallel} and the Mel'nikov–Meshkov turnover formula. Here, we see the asymmetry effect alluded to in the Introduction where for a certain value of h , namely, $h_c \approx 0.18$, the Arrhenius behavior (exponential increase with increasing barrier height) of the correlation time τ_{\parallel} disappears. Such an effect occurs at a critical value h_c of the ratio h , that is, bias field parameter/anisotropy barrier height parameter, *far less* than the nucleation field, which is the value needed to destroy the bistable nature of the potential. Thus in the low-temperature limit, the overall relaxation process is no longer dominated by the slow decay or interwell mode associated with the barrier crossing at values of h in excess of the critical value. The phenomenon was first discovered (numerical methods) by Coffey et al. [83] and later explained by Garanin [84] for the very similar problem of the magnetization relaxation of a uniaxial superparamagnetic particle subjected to a dc magnetic field. Garanin [84] showed that this effect is a natural consequence of the population depletion of the shallower of the two potential wells (which are involved in

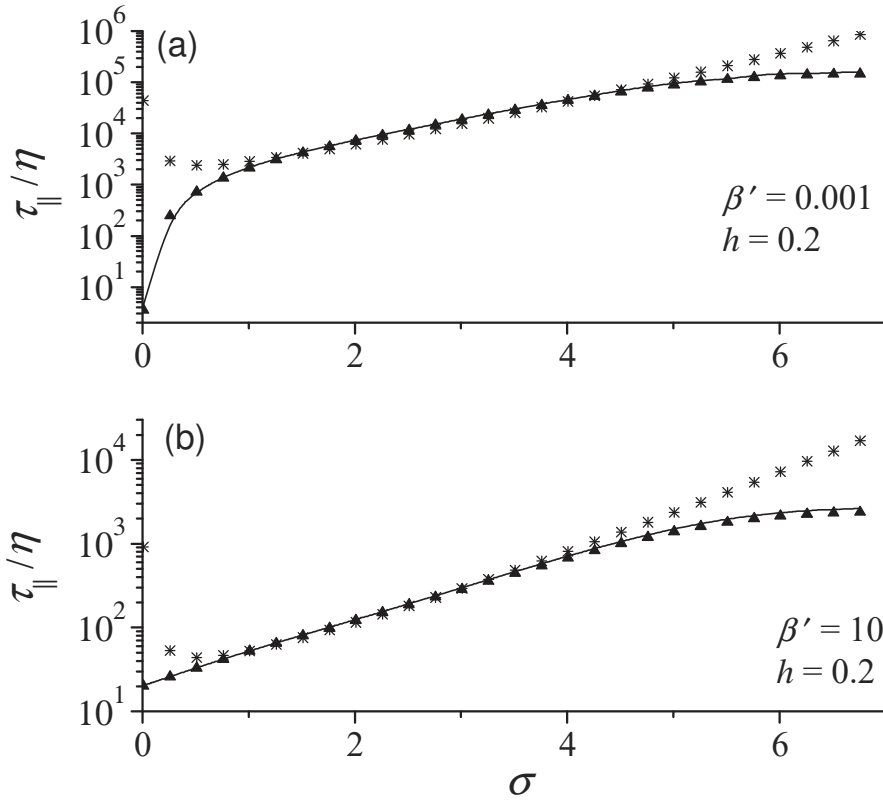


Figure 11. τ_{\parallel}/η versus σ for $\beta' = 0.001$ (a; very low damping) and $\beta' = 10$ (b; high damping). Solid lines: exact matrix continued fraction solution for the correlation time τ_{\parallel} ; stars: the Mel'nikov–Meshkov equation (196); triangles: Eqs. (202) and (206) for the VHD and VLD regions, respectively.

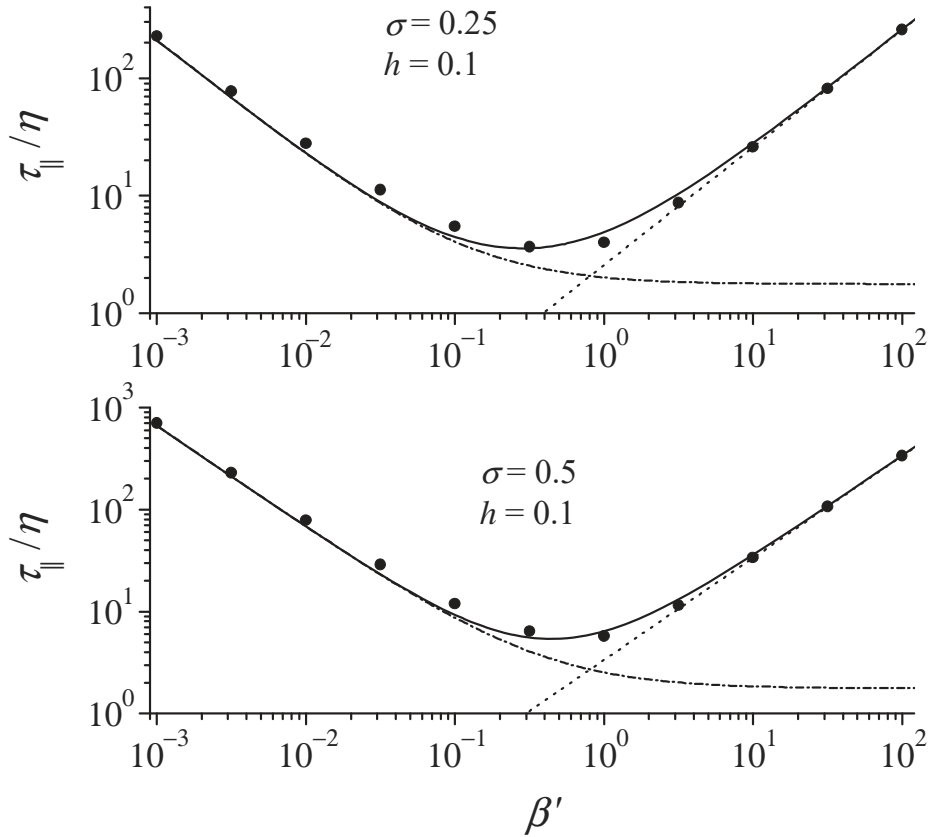


Figure 12. τ_{\parallel}/η versus β' for small barrier heights $\sigma = 0.25$ and 0.5 , and $h = 0.1$. Filled circles: exact matrix continued fraction solution for the correlation time τ_{\parallel} , dashed-dotted lines 2: the VLD Eq. (206); dotted lines 3: the VHD Eq. (202); solid lines 1: Eq. (181).

the barrier crossing) by the uniform field. Essentially when a significant part of the population of the shallow well has descended to the deeper well the enhanced population in that well cannot escape because of the high-potential barrier that it must overcome. Further in Ref. [88], it has been shown that this depletion effect always exists in relaxation in bistable potentials and it has also been asserted [14] that such an effect is a general feature of relaxation in biased double-well potentials. In the particular application here, the long time behavior of $C(t)$ at low temperatures ($\sigma, \xi \gg 1$) may be approximated by two exponentials corresponding to overbarrier and intrawell relaxation processes (on neglecting the contribution of librational modes)

$$C(t) \approx (1 - \Delta_1) e^{-t\lambda_1} + \Delta_1 e^{-t/\tau_{\text{well}}} \quad (209)$$

where τ_{well} is the effective relaxation time in the deep well and so has a weak temperature dependence. According to Eqs. (162) and (209),

$$\tau_{\parallel} \approx (1 - \Delta_1)\lambda_1^{-1} + \Delta_1\tau_{\text{well}} \quad (210)$$

If $h < h_c$, the quantity $(1 - \Delta_1)\lambda_1^{-1}$ increases exponentially as the temperature T decreases and so $(1 - \Delta_1)\lambda_1^{-1}$ determines completely the temperature dependence of the correlation time τ_{\parallel} . While with $h > h_c$, the quantity $(1 - \Delta_1)\lambda_1^{-1}$ decreases exponentially as T decreases (due to the depletion effect $(1 - \Delta_1)\lambda_1^{-1}$ is exponentially small in spite of the fact that λ_1^{-1} is exponentially large), thus τ_{\parallel} no longer has Arrhenius behavior and now differs exponentially from λ_1^{-1} . Thus for $h = h_c$, the relaxation switches from being dominated by the behavior of the longest lived relaxation mode associated with λ_1^{-1} that is the inverse Kramers escape rate to being dominated by the fast relaxation processes in the deep well of the potential because of the depletion of the upper (shallow) well at low temperatures [84,88].

In Fig. 12, we compare the VHD and VLD correlation time equations (202) and (206) with the exact numerical solution for the correlation time at small barriers. Here, the simple *ad hoc* extrapolating Eq. (181) [2] provides a satisfactory estimate of the correlation time τ_{\parallel} for all damping and also the longest relaxation time provided $h < h_c$ because then $\tau_{\parallel} \approx \lambda_1^{-1}$. We emphasize that Eqs. (202), (206), and (181) can be used for *all barrier heights* σ , where the turnover formula is not applicable.

Thus, the turnover formula [8,10], Eq. (196), for the longest relaxation time bridging the VLD and IHD escape rates as a function of the dissipation parameter β' yields satisfactory agreement with the numerical results for fixed axis rotators in an asymmetrical double-well potential for all values of β' . Equation (196) allows one also to accurately estimate the damping dependence of the low-frequency part of the spectra of the equilibrium correlation function $C(t)$ and of the longitudinal

complex susceptibility $\chi(\omega)$. Moreover, one may estimate the contribution of the overbarrier relaxation mode to the correlation time τ_{\parallel} .

F. Escape Rate for a Translational Brownian Particle in a Double-Well Potential

1. Langevin Equation Approach

The translational Brownian motion in a (2–4) double-well potential

$$V(x) = \frac{1}{2}ax^2 + \frac{1}{4}bx^4, \quad -\infty < x < \infty \quad (211)$$

where a and b are constants, is almost invariably used to describe the noise driven motion in bistable physical and chemical systems. Examples are fields as diverse as simple isometrization processes [89–93], chemical reaction rate theory [15,33,94–100], bistable nonlinear oscillators [101–103], second-order phase transitions [104], nuclear fission and fusion [105,106]. The number of papers devoted to the problem is enormous and many methods of solution have been presented because the stochastic dynamics of barrier-crossing transitions is of fundamental significance in physics [62,70,107–110].

Here, we apply the turnover formula to the analysis of the dynamics of a Brownian particle in the double-well potential given by Eq. (211). The dynamics of this system in the VHD limit, where the inertia of the particle may be neglected, have been extensively studied either by using the Kramers escape rate theory [2,15] or by solution of the appropriate Smoluchowski equation (see, e.g. [111–114] and references cited therein). In the VHD limit, the analysis has habitually proceeded from the Smoluchowski equation either by converting the solution of that equation to a Sturm–Liouville problem (e.g. [111,112]) or by the solution of an infinite hierarchy of linear differential–recurrence relations for statistical moments (e.g. [113,114]). However, we saw that Coffey and coworkers [113] (see also [14]) have formulated an analytical method of finding exact solutions of differential–recurrence relations for statistical moments by using continued fractions. The method allows us to calculate in closed form the correlation times, the spectra of the correlation functions and the generalized susceptibilities for the relevant dynamical variables [14,113]. Yet another method of solution has been proposed by Perico et al. [114]. They used the mean first passage time to derive an integral expression for the correlation time defined, as usual, as the area under the curve of the positional autocorrelation function. By applying the Mori memory function formalism, they were also able to calculate the position correlation function and to compare it with various approximate formulas and computer simulations. If the inertial effects are taken into account, a large number of special solutions exist mostly for particular observables. For example, in the

low-temperature limit, the transition rate from one well to another is of special interest and can be given analytically while some results for the longest relaxation time have been obtained via escape rate theory, for example, in Refs [48,115,116]. The position correlation function $C(t) = \langle x(0)x(t) \rangle_0 / \langle x^2(0) \rangle_0$ (the symbol $\langle \rangle_0$ denotes the equilibrium ensemble averages) and its spectra for both low and very low damping were treated in Refs [102,117–119]. Fourier transforms of correlation functions have also been obtained in Refs [120,121] by a projection operator method. Furthermore, Voigtlaender and Risken [122] calculated eigenvalues and eigenfunctions of the Klein–Kramers (Fokker–Planck) equation for a Brownian particle in the double-well potential Eq. (211) and evaluated the Fourier transforms of various correlation functions using matrix continued fractions [16]. The method is as follows. First the distribution function is expanded in Hermite functions with respect to the velocity as originally done by Brinkman [33] and then in Hermite functions with respect to position. Next by inserting the distribution function in this basis into the Fokker–Planck equation they obtain a recursion relation for the expansion coefficients. By introducing a suitable vector and matrix notation, this recurrence relation is then cast into a tridiagonal vector recurrence relation that is solved via matrix continued fractions. Using this method, Coffey et al. [52] have presented a detailed comparison of the turnover formula results with a matrix continued fraction solution for the position correlation function and its correlation time, the smallest nonvanishing eigenvalue of the corresponding Fokker–Planck equation, and generalized dynamic susceptibility. Their matrix continued fraction solution owes much to the work of Voigtlaender and Risken [122]. However, the algorithm for the matrix continued fraction solution is simplified and optimized (it is about 10 times faster and may be applied for higher barriers and smaller damping constants than those of the original paper of Voigtlaender and Risken [122]).

We consider the one-dimensional translational Brownian motion of a particle in the double-well potential Eq. (211). The governing nonlinear Langevin equation is [122]

$$m\ddot{x}(t) + \zeta\dot{x}(t) + \frac{dV}{dx}[x(t)] = F(t) \quad (212)$$

In Eq. (212), $x(t)$ specifies the position of the particle at time t , m is the mass of the particle, $\zeta\dot{x}$ is the viscous drag experienced by it, and $F(t)$ is the white noise driving force so that

$$\overline{F(t)} = 0, \quad \overline{F(t)F(t')} = 2k_B T\zeta\delta(t - t') \quad (213)$$

Here, the overbar means the statistical average over an ensemble of particles that have all started at time t with the same initial position $x(t) = x$ and velocity $\dot{x}(t) = \dot{x}$. Equation (212) is interpreted here as a stochastic differential equation of the Stratonovich type [14,16]. Though the nonlinearity alters the motion of $x(t)$, many

features of the linear equation with $a > 0$ and $b = 0$ still remain for $b > 0$ $a > 0$ [now the potential Eq. (211) has only one minimum]. For $b > 0$ and $a < 0$, Eq. (211) (representing a Duffing oscillator potential) has two minima at $x_{1,2} = \pm\sqrt{-a/b}$ separated by a maximum at $x_0 = 0$ and the motion $x(t)$ strongly deviates from the linear case. Thus for small energies, the particle oscillates either in the left or in the right well. However even weak noise ensures that the particles do not stay in the same well, they now have a chance to go in the opposite direction, so that particles from the left well may finally reach the right well and vice versa.

The appropriate Klein–Kramers (Fokker–Planck) equation for the joint PDF $W(x, \dot{x}, t)$ of the phase space variables x and \dot{x} may be written [122]

$$\frac{\partial W}{\partial t} = L_{\text{FP}} W \quad (214)$$

where the Fokker–Planck operator L_{FP} is given by

$$L_{\text{FP}} W = -\dot{x} \frac{\partial W}{\partial x} + \frac{1}{m} \frac{dV}{dx} \frac{\partial W}{\partial \dot{x}} + \frac{\zeta}{m} \left(\frac{\partial}{\partial \dot{x}} (\dot{x} W) + \frac{k_{\text{B}} T}{m} \frac{\partial^2 W}{\partial \dot{x}^2} \right) \quad (215)$$

By introducing dimensionless variables and parameters as in [14,114]

$$y = \frac{x}{\langle x^2 \rangle_0^{1/2}}, \quad A = \frac{a \langle x^2 \rangle_0}{2k_{\text{B}} T}, \quad B = \frac{b \langle x^2 \rangle_0^2}{4k_{\text{B}} T}, \quad \beta' = \eta \frac{\zeta}{m} \quad (216)$$

where $\eta = \sqrt{m \langle x^2 \rangle_0 / (2k_{\text{B}} T)}$ is a characteristic time, Eq. (212) now becomes

$$\eta^2 \ddot{y}(t) + \eta \beta' \dot{y}(t) + Ay(t) + 2By^3(t) = \frac{\eta}{\sqrt{2mk_{\text{B}} T}} \lambda(t) \quad (217)$$

The normalization condition $\langle y^2 \rangle_0 = 1$ implies that the constants A and B are not independent [114]

$$B = B(Q) = \frac{1}{8} \left[\frac{D_{-3/2}(\text{sgn}(A)\sqrt{2Q})}{D_{-1/2}(\text{sgn}(A)\sqrt{2Q})} \right]^2 \quad (218)$$

where $Q = A^2/4B$ and the $D_\nu(z)$ are parabolic cylinder functions of order ν [72]. For $A < 0$ (which is the case of greatest interest), Q is equal to the barrier height for the potential $V(y) = Ay^2 + By^4$ (see Fig. 13). For $A < 0$ and small Q [123]

$$B = 0.1142 + 0.1835\sqrt{Q} + \dots$$

while for $A < 0$ and $Q \gg 1$, $B \sim Q$.

Now the relevant quantities are the position autocorrelation function

$$C(t) = \langle y(0)y(t) \rangle_0 \quad (219)$$

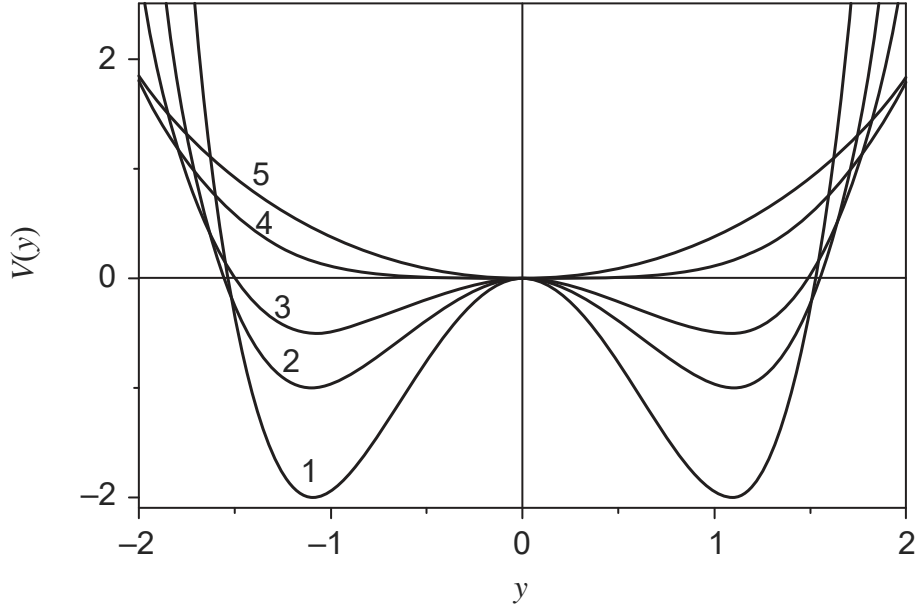


Figure 13. Potential $V(y) = Ay^2 + By^4$ for various values of $A/(2B^{1/2}) = -2^{1/2}$ (curve 1), $-1(2)$, $-2^{-1/2}(3)$, $0(4)$ and $1(5)$.

and the correlation time T_c , which is again a global characteristic of the relaxation process involved and is defined as the area under the curve of $C(t)$, namely [14,16]

$$T_c = \int_0^{\infty} C(t) dt \quad (220)$$

because $C(0) = 1$ due to the normalization conditions. According to linear response theory (see, e.g. [14,16] having determined the one-sided Fourier transform $\tilde{C}(\omega)$ [the spectrum of the equilibrium correlation function $C(t)$], one can calculate the normalized dynamic susceptibility $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$ [122]

$$\chi(\omega) = 1 - i\omega\tilde{C}(\omega) \quad (221)$$

Once again by utilizing general properties of Fourier transforms, we may also obtain simple asymptotic equations for $\chi(\omega)$ in the low- and high-frequency limits. We have

$$\chi''(\omega) \sim \omega \int_0^{\infty} C(t) dt + \dots = \omega T_c \quad (222)$$

for $\omega \rightarrow 0$, and

$$\frac{\chi''(\omega)}{\chi'(0)} \sim \frac{\ddot{C}(0)}{\omega^3} + \dots \quad (223)$$

for $\omega \rightarrow \infty$ (because $\dot{C}_{\parallel}(0) = 0$).

The correlation time T_c may also be defined in terms of the eigenvalues (λ_k) of the Fokker–Planck operator L_{FP} [cf. Eq. (164)]

$$T_c = \sum_k c_k / \lambda_k \quad (224)$$

where $\sum_k c_k = 1$, which again contains contributions from *all* the eigenvalues λ_k . As we have seen, for equivalent wells, the approximation $T_c \approx \lambda_1^{-1}$ can be used. In other words, the inverse of the smallest nonvanishing eigenvalue, that is, the longest relaxation time, closely approximates the correlation time T_c for symmetrical potentials in the low-temperature (high-barrier) limit.

As shown in Ref. [52], by applying the general method of solution of nonlinear Langevin equations developed by Coffey et al. [14] one may recast Eq. (217) as a hierarchy of differential–recurrence equations for the correlation functions (observables) $c_{n,q}(t)$ defined as

$$c_{n,q}(t) = \frac{1}{\sqrt{2^{n+q} n! q!}} \langle y(0) H_q [\alpha B^{1/4} y(t)] H_n [\eta \dot{y}(t)] e^{[-\alpha^2 B^{1/2} y^2(t) + A y^2(t) + B y^4(t)]/2} \rangle_0 \quad (225)$$

where $y(0)$ is the initial value of $y(t)$, and α is a scaling factor with value chosen so as to ensure convergence of the continued fractions involved as suggested by Voigtlaender and Risken [122] (all results for the observables such as λ_1 and T_c are independent of α). The hierarchy has the form [52]

$$\begin{aligned} \frac{d}{dt'} c_{n,q}(t) + \beta' n c_{n,q}(t) = & \sqrt{n+1} [e_q c_{n+1,q+3}(t) + d_q^- c_{n+1,q+1}(t) \\ & + d_{q-1}^+ c_{n+1,q-1}(t) + e_{q-3} c_{n+1,q-3}(t)] \\ & - \sqrt{n} [e_q c_{n-1,q+3}(t) + d_q^+ c_{n-1,q+1}(t) \\ & + d_{q-1}^- c_{n-1,q-1}(t) + e_{q-3} c_{n-1,q-3}(t)] \end{aligned} \quad (226)$$

where

$$d_q^\pm = \frac{B^{1/4}}{2\alpha^3} \sqrt{q+1} [3(q+1) - 2\alpha^2 \sqrt{Q} \pm \alpha^4] \quad (227)$$

$$e_q = \frac{B^{1/4}}{2\alpha^3} \sqrt{(q+3)(q+2)(q+1)} \quad (228)$$

The initial conditions for $c_{n,q}(t)$ are given by

$$\begin{aligned} c_{0,2q-1}(0) &= \frac{1}{\sqrt{2^{2q-1}(2q-1)!}} \langle y H_{2q-1}(\alpha B^{1/4} y) e^{(-\alpha^2 B^{1/2} y^2 + Ay^2 + By^4)/2} \rangle_0 \\ &= \frac{1}{Z \sqrt{2^{2q-1}(2q-1)! B}} \int_{-\infty}^{\infty} \xi H_{2q-1}(\alpha \xi) e^{-(\alpha^2 \xi^2 - 2\sqrt{Q}\xi^2 + \xi^4)/2} d\xi \end{aligned} \quad (229)$$

where the partition function Z is given by [114]

$$Z = \int_{-\infty}^{\infty} e^{-Ay^2 - By^4} dy = \sqrt{\pi} (2B)^{-1/4} e^{Q/2} D_{-1/2}(-\sqrt{2Q}) \quad (230)$$

Note that $c_{n,q}(0) = 0$ for $n \geq 1$ and $c_{0,2q}(0) = 0$ for the equilibrium Maxwell–Boltzmann distribution. Equation (226) (originally derived by Voigtlaender and Risken [122] from the Fokker–Planck equation) is the desired recurrence equation for the statistical moments that can be solved by the matrix continued fraction method [14,16].

Here, we briefly describe an algorithm for the continued fraction solution that is faster (by a factor of about 10) and more stable [52] than that used by Voigtlaender and Risken [122]. First we note that the recurrence equation (226) may be separated in two independent systems with $q+n$ even and odd. In order to solve Eq. (226) for $q+n$ even, we introduce the column vectors

$$\mathbf{C}_{2n-1}(t) = \begin{pmatrix} c_{2n-2,1}(t) \\ c_{2n-2,3}(t) \\ \vdots \end{pmatrix}, \quad \mathbf{C}_{2n}(t) = \begin{pmatrix} c_{2n-1,0}(t) \\ c_{2n-1,2}(t) \\ \vdots \end{pmatrix}, \quad (n \geq 1) \quad (231)$$

Now, Eq. (226) can be rearranged as usual as the set of matrix *three-term* recurrence equations

$$\eta \frac{d}{dt} \mathbf{C}_n(t) = \mathbf{Q}_n^- \mathbf{C}_{n-1}(t) - \beta'(n-1) \mathbf{C}_n(t) + \mathbf{Q}_n^+ \mathbf{C}_{n+1}(t) \quad (232)$$

where the matrices \mathbf{Q}_n^+ and \mathbf{Q}_n^- are infinite four-diagonal matrices. Their matrix elements are given by

$$\begin{aligned} [\mathbf{Q}_{2n-m}^\pm]_{p,q} &= \pm \sqrt{2n-m - \frac{1 \mp 1}{2}} (\delta_{pq+2-m} e_{2p-5+m} + \delta_{pq+1-m} d_{2p-3+m}^\pm \\ &\quad + \delta_{pq-m} d_{2p-2+m}^\mp + \delta_{pq-1-m} e_{2p-2+m}) \end{aligned} \quad (233)$$

($p, q \geq 1$). By one-sided Fourier transformation, we have from Eq. (226)

$$[i\eta\omega + \beta'(n-1)] \tilde{\mathbf{C}}_n(\omega) - \mathbf{Q}_n^+ \tilde{\mathbf{C}}_{n+1}(\omega) - \mathbf{Q}_n^- \tilde{\mathbf{C}}_{n-1}(\omega) = \eta\delta_{n1} \mathbf{C}_1(0) \quad (234)$$

where the elements of the column vector $\mathbf{C}_1(0)$ are defined by Eq. (226).

Again invoking the general method [14] for solving the matrix recurrence equation (234), we have the exact solution for $\tilde{\mathbf{C}}_1(s)$ in terms of a matrix continued fraction, namely,

$$\tilde{\mathbf{C}}_1(\omega) = \eta \Delta_1(i\omega) \mathbf{C}_1(0) \quad (235)$$

where $\Delta_n(s)$ is defined by the recurrence equation

$$\Delta_n(i\omega) = \left\{ [i\eta\omega + \beta'(n-1)] \mathbf{I} - \mathbf{Q}_n^+ \Delta_{n+1}(s) \mathbf{Q}_{n+1}^- \right\}^{-1} \quad (236)$$

where \mathbf{I} is the unit matrix. Having determined $\tilde{\mathbf{C}}_1(\omega)$, we can evaluate the spectrum of the position correlation function $C(t) = \langle y(0)y(t) \rangle_0$, Eq. (219), in terms of $c_{0,q}(t)$ via

$$\begin{aligned} C(t) &= \sum_{q=0}^{\infty} a_q c_{0,q}(t) \\ &= \sum_{q=0}^{\infty} a_q \frac{1}{\sqrt{2^q q!}} \langle y(0) H_q [\alpha B^{1/4} y(t)] e^{[-\alpha^2 B^{1/2} y^2(t) + A y^2(t) + B y^4(t)]/2} \rangle_0 \end{aligned} \quad (237)$$

where, due to the orthogonality properties of the Hermite polynomials, $a_{2q} = 0$ and

$$\begin{aligned} a_{2q-1} &= \frac{\alpha B^{1/4}}{\sqrt{\pi 2^{2q-1} (2q-1)!}} \int_{-\infty}^{\infty} y H_{2q-1}(\alpha B^{1/4} y) e^{-(\alpha^2 B^{1/2} y^2 + A y^2 + B y^4)/2} dy \\ &= c_{0,2q-1}(0) \frac{\alpha Z B^{1/4}}{\sqrt{\pi}} \end{aligned}$$

Thus, the one-sided Fourier transform of $C(t)$ is given by

$$\tilde{C}(\omega) = \frac{\eta \alpha Z B^{1/4}}{\sqrt{\pi}} \mathbf{C}_1^T(0) \Delta_1(i\omega) \mathbf{C}_1(0) \quad (238)$$

where the sign “T” (transpose) designates transformation of a column vector to a row vector. According to Eq. (220), the correlation time T_c is now given by

$$T_c = \tilde{C}(0) = \frac{\eta\alpha Z B^{1/4}}{\sqrt{\pi}} \mathbf{C}_1^T(0) \mathbf{\Delta}_1(0) \mathbf{C}_1(0) \quad (239)$$

Noting Eq. (232) and that $\mathbf{C}_n(0) = \mathbf{0}$ for $n > 1$, one can show that $\ddot{\mathbf{C}}_1(0) = -\beta' \eta^{-3} \mathbf{Q}_1^+ \mathbf{Q}_2^- \mathbf{C}_1(0)$ so that the third derivative of the correlation function $C(t) = (\alpha Z B^{1/4} / \sqrt{\pi}) \mathbf{C}_1^T(0) \mathbf{C}_1(t)$ is

$$\ddot{C}(0) = \langle y(0) \ddot{y}(0) \rangle_0 = \frac{\alpha Z B^{1/4}}{\sqrt{\pi}} \mathbf{C}_1^T(0) \ddot{\mathbf{C}}_1(0) = -\frac{\beta' \alpha Z B^{1/4}}{\eta^3 \sqrt{\pi}} \mathbf{C}_1^T(0) \mathbf{Q}_1^+ \mathbf{Q}_2^- \mathbf{C}_1(0) \quad (240)$$

Equation (240) allows one to estimate the high-frequency behavior of the susceptibility $\chi(\omega)$ from the expansion given by Eq. (223). The smallest nonvanishing eigenvalue λ_1 of the Fokker–Planck operator [that is λ_1 of the hierarchy of Eq. (226)] can also be estimated by using matrix continued fractions from the secular equation [14,16,122]

$$\det [\lambda_1 \eta \mathbf{I} + \mathbf{Q}_1 + \mathbf{Q}_1^+ \Delta_2 (-\lambda_1) \mathbf{Q}_2^-] = 0 \quad (241)$$

The *exact* matrix continued fraction solution is again easily computed. Again as far as practical calculations of the infinite matrix continued fraction are concerned, we approximate it by a matrix continued fraction of finite order (by putting $\mathbf{\Delta}_{n+1} = \mathbf{0}$ at some $n = N$); simultaneously, we confine the dimensions of the infinite matrices \mathbf{Q}_n^- , \mathbf{Q}_n^+ , and \mathbf{I} to a finite value $M \times M$. N and M were determined in such way that a further increase of N and M did not change the results. Both N and M depend on the dimensionless barrier (Q) and damping (β') parameters and must be chosen taking into account the desired degree of accuracy of the calculation. The final results are independent of the scaling factor α . The advantage of choosing an optimum value of α is, however, that the dimensions N and M can then be minimized [122]. Both N and M increase with decreasing β' and increasing Q .

The relaxation times T_c and $1/\lambda_1$ yielded by the matrix continued fraction method will now be compared with those obtained by the turnover formula.

2. Turnover Formula

The turnover formula for the potential of Eq. (211) yields [52]

$$\tau = \frac{A(2\Delta)}{A^2(\Delta)} \tau_{\text{IHD}} \quad (242)$$

where the depopulation factor $A(\Delta)$ is given by Eq. (24) with $\Delta = \beta' S / (\eta k_B T)$, where $S = \oint_{\text{well}} \sqrt{-2mV(x)} dx$ is the action in the well that can be calculated as

$$S = 2 \int_{x'_2}^0 \sqrt{-2mV(x)} dx = 2 \int_0^{x'_1} \sqrt{-2mV(x)} dx = k_B T \eta \frac{8\sqrt{2}Q^{3/4}}{3B^{1/4}}$$

Here, $x'_{1,2} = \pm (4\langle x^2 \rangle_0^2 Q/B)^{1/4}$ are the solutions of the equation $V(x) = 0$. For $Q \gg 1$, $S \sim (8/3)k_B T \eta \sqrt{2}Q$. The time τ_{IHD} is the longest relaxation time for IHD damping ($\beta' \geq 1$) defined as $\tau_{\text{IHD}}^{-1} = \Gamma_1^{\text{IHD}} + \Gamma_2^{\text{IHD}} = 2\Gamma_1^{\text{IHD}}$, where Γ_1^{IHD} and Γ_2^{IHD} are the Kramers escape rates from the wells 1 and 2, respectively (due to the equivalence of the wells 1 and 2, $\Gamma_1^{\text{IHD}} = \Gamma_2^{\text{IHD}}$), so that

$$\begin{aligned} \tau_{\text{IHD}}^{-1} &= \frac{1}{2\pi\eta} \left[\sqrt{\frac{\beta'^2}{4} + \frac{\eta^2}{m} |V''(0)|} - \frac{\beta'}{2} \right] \left[\sqrt{\frac{V''(x_1)}{|V''(0)|}} e^{V(x_1)/(k_B T)} + \sqrt{\frac{V''(x_2)}{|V''(0)|}} e^{V(x_2)/(k_B T)} \right] \\ &= \frac{e^{-Q}}{\sqrt{2}\pi\eta} \left(\sqrt{\beta'^2 + 8\sqrt{QB}} - \beta' \right) \end{aligned} \quad (243)$$

where $x_{1,2} = \pm \sqrt{-a/b}$ are coordinates of the minima and we have noted that $V(x_i)/(k_B T) = -Q$, $(\eta^2/m) |V''(0)| = 2\sqrt{QB}$, and $(\eta^2/m)V''(x_i) = 4\sqrt{QB}$. The leading factor on the right-hand side of Eq. (242) is the correction to the IHD result due to Mel'nikov and Meshkov (the depopulation factor).

If $\beta' \rightarrow \infty$, we have from Eqs. (120) and (242) the VHD formula

$$\tau_{\text{VHD}} = \frac{\pi\eta\beta'}{2\sqrt{2}Q} e^Q \quad (244)$$

which is the result of Larsson and Kostin [107] (in our notation). In like manner, in the VLD limit ($\beta' \rightarrow 0$), we have

$$\tau_{\text{VLD}} = \frac{3\pi\eta}{8\sqrt{2}\beta'Q} e^Q \quad (245)$$

The longest relaxation time τ yielded by the asymptotic Eqs. (242), (243)–(245) will be compared with that evaluated from the matrix continued fraction solution below.

3. Correlation Time in the VHD and VLD Limits

As before the correlation time T_c can be calculated from Eq. (174) so that we can again obtain accurate VHD and VLD asymptotes from Eq. (174). In the VHD

limit ($\beta' \gg 1$), the appropriate single variable Smoluchowski equation for the PDF $W(y, t)$ is [114]

$$\frac{\partial W}{\partial t} = \frac{1}{2\beta'\eta} \frac{\partial}{\partial y} \left(\frac{\partial}{\partial y} + 2Ay + 4By^3 \right) W \quad (246)$$

Because $D^{(2)}(y) = 1/(2\beta'\eta)$, the correlation time T_c of the position autocorrelation function $C(t)$ is given by the general equation (174), so that [114]

$$T_c = T^{\text{VHD}} = 2\eta\beta' \int_{-\infty}^{\infty} \frac{1}{W_{\text{st}}(y)} \left[\int_{-\infty}^y y' W_{\text{st}}(y') dy' \right]^2 dy \quad (247)$$

Here, $W_{\text{st}}(y) = e^{-Ay^2 - By^4}/Z$ is the equilibrium Boltzmann distribution function [which is a stationary solution of Eq. (246)]. For $A < 0$, we have by changing the variables in Eq. (247)

$$\frac{T_c}{\eta} = \beta' \frac{2^{1/4} \sqrt{\pi} e^{Q/2} D_{-1/2}(-\sqrt{2Q})}{[D_{-3/2}(-\sqrt{2Q})]^2} \int_{-\sqrt{Q}}^{\infty} \frac{e^{x^2} [1 - \text{erf}(x)]^2}{\sqrt{x + \sqrt{Q}}} dx \quad (248)$$

where we have used

$$\int_{-\infty}^y y' e^{-Ay'^2 - By'^4} dy' = \frac{\sqrt{\pi/B}}{4} e^{A^2/4B} [\text{erf}(\sqrt{B}y^2 + A/2\sqrt{B}) - 1]$$

In the opposite low damping limit ($\beta' \ll 1$), one may in order to obtain a single variable Fokker–Planck equation introduce the energy of the dipole

$$\varepsilon = \eta^2 \dot{y}^2 + Ay^2 + By^4 \quad (249)$$

and the time w (phase) measured along a closed trajectory in phase space as action–angle variables [2,15]. The energy ε varies very slowly with time. Consequently, it is a slow variable in comparison to the phase w . Again by using the method of Praestgaard and van Kampen [69], that is, averaging the Fokker–Planck equation (214) over the fast phase variable w , we have a single variable Fokker–Planck equation for the PDF $W(\varepsilon, t)$ in energy space

$$\frac{\partial W}{\partial t} = \frac{2\beta'}{\eta} \left[\frac{\partial}{\partial \varepsilon} \left(\eta^2 \overline{\dot{y}^2}(\varepsilon) - \frac{1}{2} \right) + \eta^2 \frac{\partial^2}{\partial \varepsilon^2} \overline{\dot{y}^2}(\varepsilon) \right] W \quad (250)$$

where the double overbar denotes averaging over the fast phase variable. Now T_c is given by

$$T_c \approx T^{\text{VLD}} = \int_{-Q}^{\infty} \frac{1}{D^{(2)}(\varepsilon) W_{\text{st}}(\varepsilon)} \left[\int_{-Q}^{\varepsilon} \overline{\overline{y}}(\varepsilon') W_{\text{st}}(\varepsilon') d\varepsilon' \right]^2 d\varepsilon \quad (251)$$

where the diffusion coefficient $D^{(2)}(\varepsilon)$ is given by

$$D^{(2)}(\varepsilon) = 2\beta' \eta \overline{\overline{y^2}}(\varepsilon) = 2\beta' \eta^{-1} \left[\varepsilon - A \overline{\overline{y^2}}(\varepsilon) - B \overline{\overline{y^4}}(\varepsilon) \right]$$

By calculating the integrals in Eq. (251) as described in Appendix C.3, we obtain

$$T^{\text{VLD}} = \frac{3\pi\eta 2^{7/4} e^{Q/2} Q^{1/4}}{\beta' D_{-3/2}(-\sqrt{2}Q)} \int_0^1 \frac{x \sinh^2(Qx^2/2)}{\sqrt{1+x} \{E[2x/(1+x)] - (1-x)K[2x/(1+x)]\}} dx \quad (252)$$

where $K(m)$ and $E(m)$ are complete elliptic integrals of the first and second kind, respectively [72].

The merit of Eqs. (248) and (252) is that as before they yield VHD and VLD asymptotes for T_c valid for *all barrier heights* including *low barriers* ($Q \leq 1$), where asymptotic methods (like the turnover equation) are not applicable.

4. Comparison of the Exact and Approximate Approaches

The longest relaxation time τ predicted by the turnover equation (242) and the smallest nonvanishing eigenvalue λ_1 calculated numerically by matrix continued fraction methods are shown in Fig. 14 as functions of β' for relatively high values of the barrier height parameter $Q = 5$ and 10. Here, the VHD [Eq. (244)], IHD [Eq. (243)], and VLD [Eq. (245)] asymptotes for τ are also shown for comparison. Apparently in the high-barrier limit, Eq. (242) provides a good approximation to λ_1 for all β' including the VHD, VLD, and turnover regions. The quantitative agreement in damping behavior may be explained as follows. The behavior of the escape rate as a function of the barrier height parameter Q for large Q is again approximately Arrhenius-like and arises from an *equilibrium* property of the system (namely the Boltzmann distribution at the bottom of the well). On the other hand, the damping dependence of the escape rate is again due to *nonequilibrium* (dynamical) properties of the system and so is contained in the prefactor A only, the detailed nature of which depends on the behavior of the energy distribution function at the barrier points [3].

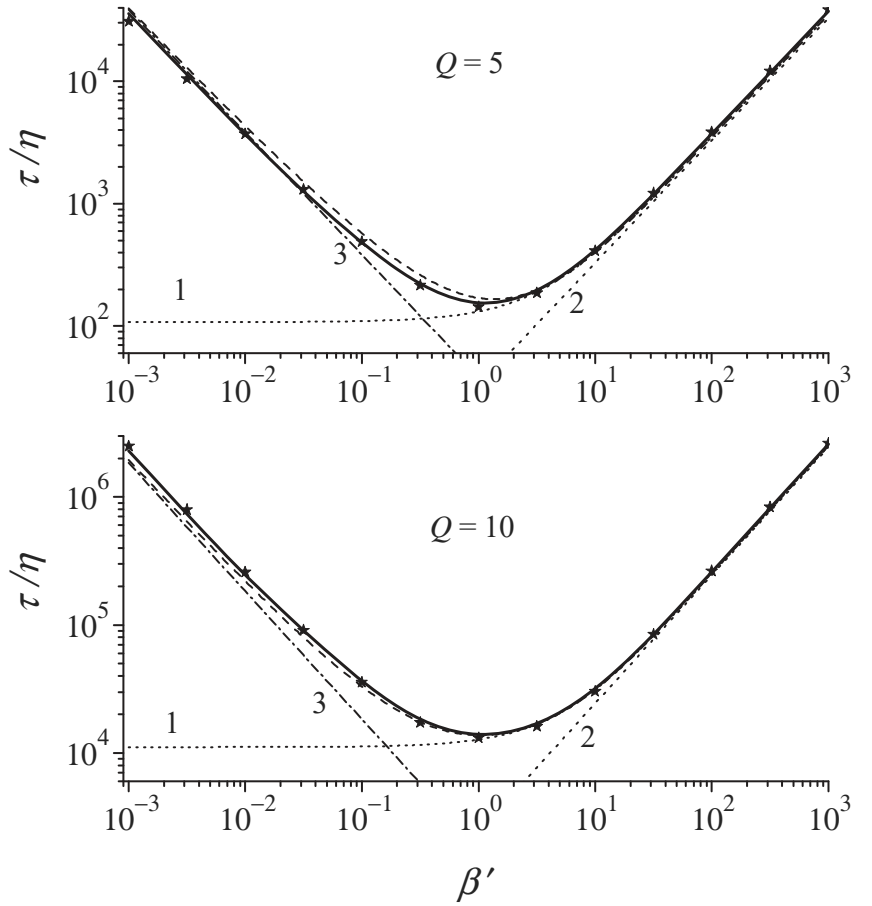


Figure 14. τ/η versus β' for $Q=5$ and 10 . Solid line: exact solution, Eq. (239); dashed line: the Mel'nikov–Meshkov equation (242); dotted line 1: the IHD Eq. (243); dotted line 2: the VHD Eq. (244); dashed-dotted line 3: the VLD Eq. (245); stars: $(\eta\lambda_1)^{-1}$ from Eq. (241).

In Fig. 15, we compare the VLD and VHD asymptotes of T_c , Eqs. (245) and (244), with the turnover equation (242) and numerical solutions for T_c and the inverse of the smallest nonvanishing eigenvalue λ_1 for low ($\beta' = 0.001$) and high ($\beta' = 10.0$) values of damping. Clearly, the turnover formula provides a good approximation both for T_c and $1/\lambda_1$ at $Q > 2$. In Fig. 16, we compare the VHD and VLD correlation times, Eqs. (248) and (252), with the exact numerical solution for T_c and $1/\lambda_1$ at small barriers, $Q = 0.5$, where the turnover formula is inapplicable. Equations (248) and (252) may be used to estimate T_c for $\beta' \gg 1$ and $\beta' \ll 1$, respectively, and for *all barrier heights* Q including very low barriers. We also remark that for intermediate and high damping, $\beta' \geq 1$, the numerical values of $1/\lambda_1$ and T_c are very close to each other while for low damping, $\beta' \ll 1$, $1/\lambda_1$ differs considerably from T_c .

The imaginary $\chi''(\omega)$ part of the dynamic susceptibility for various values of the barrier height Q and the friction coefficient β' are shown in Fig. 17. The low- and high-frequency asymptotes [Eqs. (222) and (223)] are also shown in Fig. 17 for comparison. One relaxation band dominates the low-frequency part of the spectra and is due to the slow overbarrier relaxation of the particles in the double-well potential. As seen in Fig. 17, the low-frequency part of the spectrum may be approximated by the Debye equation, Eq. (208). Here, the characteristic frequency $\omega_R = \lambda_1 = \tau^{-1}$ of the low-frequency band strongly depends on Q as well as on the friction parameter β' according to Eq. (242). Regarding the barrier

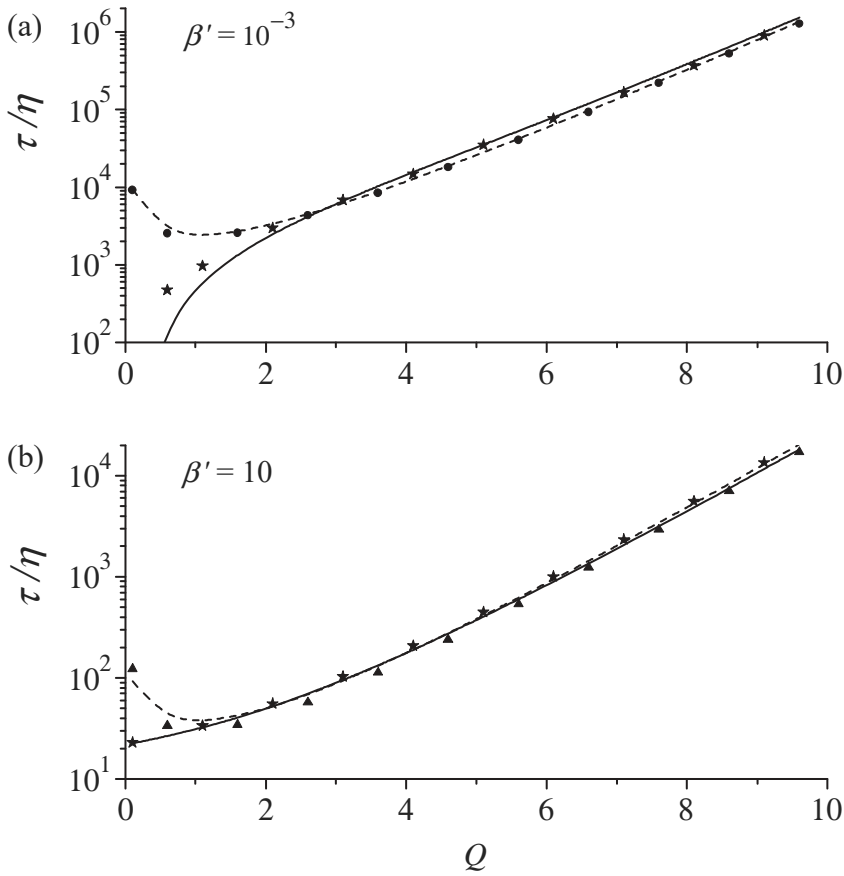


Figure 15. τ/η versus Q for $\beta' = 10^{-3}$ (a; low damping) and $\beta' = 10$ (b; high damping). Solid lines: the correlation time T_c ; dashed lines: the turnover equation (242); filled circles: the VLD Eq. (245); triangles: the VHD Eq. (244); stars: $(\eta\lambda_1)^{-1}$ from Eq. (241).

height dependence, the frequency ω_R decreases exponentially as Q is raised. This behavior occurs because the probability of escape of a dipole from one well to another over the potential barrier exponentially decreases with increasing Q . As far as the dependence of the low-frequency part of the spectrum for large friction (small inertial effects) $\beta' > 10$ is concerned, the frequency ω_R decreases as β'

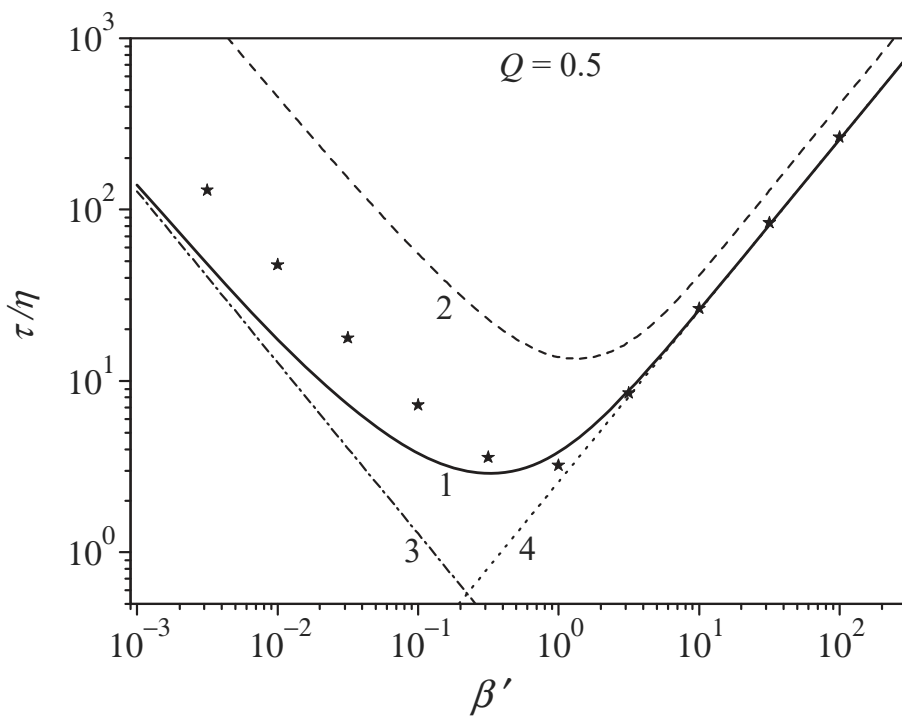


Figure 16. T_c/η versus β' for $Q = 0.5$. Solid line 1: matrix continued fraction solution; dashed line 2: the Mel'nikov–Meshkov equation (242); dashed-dotted line 3: the correlation time from the VLD Eq. (252); dotted line 4: the correlation time from the VHD Eq. (248); stars: $(\eta\lambda_1)^{-1}$ from Eq. (241).

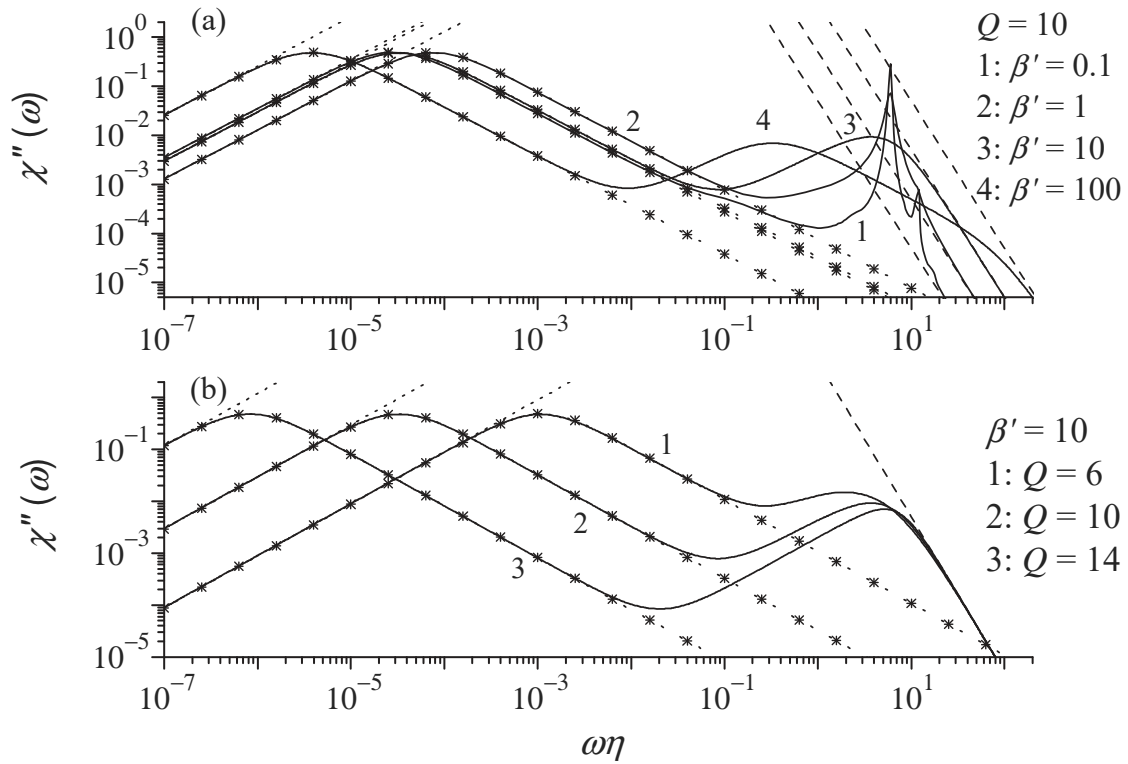


Figure 17. χ'' versus $\eta\omega$ for various values of β' and Q . Solid lines are the continued fraction solution. The Debye equation (208) with τ from Eq. (242) are shown by dotted lines with asterisks. Dotted and dashed lines: the low- and high-frequency asymptotes [Eqs. (222) and (223)].

increases as is apparent by inspection of curves in Fig. 17a. For small friction (large inertial effects) $\beta' < 0.1$, the frequency ω_R decreases with decreasing β' for given values of Q (cf. Fig. 17b). A very high-frequency band is visible in all the figures due to the fast inertial oscillations of the particles in the potential wells. For $Q \gg 1$, the characteristic frequency of oscillation ω_L increases as $\sim 2Q^{3/4}\eta^{-1}$ with increasing Q . As far as the behavior as a function of β' is concerned, the amplitude of the high-frequency band decreases progressively with increasing β' , as one would intuitively expect. On the other hand, for small friction (large inertial effects) $\beta' \ll 1$, a family of sharp resonance peaks appear in the high-frequency part of the spectra [due to resonances at the fundamental and higher harmonic frequencies of the almost free motion in the (anharmonic) potential].

Thus, we have demonstrated how the matrix continued fraction approach to the solution of nonlinear Langevin equations [14] may be successfully applied to the nonlinear Brownian oscillator in a double-well potential, Eq. (211) for wide ranges of the barrier height parameter Q and the damping parameter β' . We have shown that in the low-temperature limit, the turnover formula, Eq. (242), for the longest relaxation time bridging the VLD and IHD escape rates as a function of β' yields satisfactory agreement with the numerical results for all values of damping. Moreover, the turnover equation (242) allows one to estimate accurately the damping dependence of the low-frequency parts of the spectra of the equilibrium correlation function $C(t)$ and the complex susceptibility $\chi(\omega)$ and to evaluate the contribution

of the overbarrier relaxation mode to the correlation time T_c of the position correlation function $C(t)$. We have given an exact as well as a simple approximate analytical formula for the correlation time T_c and the dynamic susceptibility $\chi(\omega)$.

G. The Brownian Particle in a Tilted Periodic Potential

1. Applications of the Model of a Brownian Particle in a Tilted Periodic Potential

The translational Brownian motion in the tilted washboard potential

$$V(x) = -V_0 \cos(2\pi x/a) - Kx + \text{const} \quad (253)$$

where x is the position and a is a characteristic length with the constant field driving potential Kx superimposed on the periodic potential $-V_0 \cos(2\pi x/a)$, arises in a number of important physical applications involving noise and relaxation processes in phase-locked loops. We mention the current–voltage characteristics of the Josephson junction [44,124], mobility of superionic conductors [125], a laser with injected signal [126], phase-locking techniques in radio engineering [127], dielectric relaxation (when $K=0$) of molecular crystals [128], the dynamics of a charged density wave condensate in an electric field [129], ring-laser gyroscopes [130], stochastic resonance [109,131], and so on. A comprehensive discussion of the model is given in Refs [14,16,44]. Moreover, a concise method of numerical treatment (in terms of infinite continued fractions) in the VHD limit, where the inertia of the particle may be neglected, has been suggested by Cresser et al. [132]. This has particular application to a ring-laser gyroscope and has been summarized by Risken [16] (see also references cited therein). Further development of the continued fraction approach has been given by Coffey et al. [14,133].

However, the continued fraction method by its very nature precludes one from obtaining analytical expressions for important physical characteristics of the model such as the jump rate (due to thermal fluctuations) from a given well of the potential to another well arbitrarily far along the tilted washboard. Here, we shall demonstrate that the approximate solution of the Kramers escape rate problem as adopted to the potential of Eq. (253) provides in the low-temperature limit an accurate approximation for all values of the dissipation parameters to the exact jump rate (inverse jump time) yielded by the continued fraction method.

Here, we use the escape rate calculated by Mel’nikov in Refs [8,9] to analyze the dynamics of a Brownian particle in the context of the Josephson junction in the tilted periodic potential of Eq. (253) and to compare the results to the exact solutions yielded by the continued fraction method. In this way, the range of validity of the approximate analytical solution may be ascertained. Here, we recall that the Kramers problem in a tilted periodic potential is qualitatively different from the escape problem from a metastable well because the tilted periodic potential

is multistable. Thus, the particle having escaped a particular well may again be trapped due to the thermal fluctuations in another well. Moreover, jumps of either a *single* lattice spacing or of *many* lattice spacings are possible. Thus, the escape rate in a periodic potential is called the jump rate [50]. Thus from a mathematical point of view, we have to take into account the nonperiodic or running solution of the Fokker–Planck equation. Hence, the structure factor is used as described by Risken [16] to generate an additional parameter k in the Fokker–Planck equation. That parameter is then averaged over all possible jumps. Yet another difference from the conventional Kramers problem is that the stationary distribution is no longer the Maxwell–Boltzmann distribution.

In the VHD limit, the analysis of the problem usually starts from the Smoluchowski equation by either converting the solution of that equation to a Sturm–Liouville problem or to the solution of an infinite hierarchy of linear differential–recurrence relations for statistical moments [16]. We have mentioned that a concise method of numerical treatment (using infinite *scalar* continued fractions) of the periodic solution of model in the VHD limit, where the inertia of the particle may be neglected, has been suggested by Cresser et al. [132] with applications to a ring-laser gyroscope as summarized by Risken [16] (see also references cited therein). Further development of the continued fraction approach has been given by Coffey et al. [14,133]. In the opposite VLD limit, the calculation of the escape rate by Kramer’s method was accomplished in Refs [134,135]. Finally a general method of solution of the problem for all values of dissipation based on a *matrix* continued fraction representation of the Klein–Kramers equation has been suggested by Risken [16]. This method allows one to calculate eigenvalues and eigenfunctions of the Klein–Kramers (Fokker–Planck) equation for the tilted periodic potential and so evaluate the Fourier transforms of various correlation functions in virtually all cases for vanishing small damping. By applying this method, Ferrando et al. [49,50] have studied the one-dimensional translational Brownian motion in a pure periodic potential (253) with $K=0$. These authors have evaluated numerically the longest relaxation time τ from the dynamic structure factor. Moreover, the friction dependence of τ so obtained completely agrees with that yielded by the Mel’nikov turnover formula [8,9]. The treatment of the same one-dimensional problem and its generalization to diffusion on a surface has been given by Pollak et al. in Refs [54–56]. However, neither Ferrando et al. nor Pollak et al. extended their comparisons of the turnover formula with the exact solution to the tilted cosine potential that we shall now do.

We consider the one-dimensional translational Brownian motion of a particle of mass m in a tilted periodic potential (253). On introducing the normalized variable x , time t' , tilt y and barrier g parameters as

$$\frac{2\pi}{a}x \rightarrow x, \quad y = \frac{aK}{2\pi V_0}, \quad g = \frac{V_0}{k_B T}, \quad t \rightarrow \frac{t}{\eta}, \quad \eta = \frac{a}{2\pi} \sqrt{\frac{m}{2k_B T}} \quad (254)$$

the potential equation (253) takes the form

$$V(x) = -g(\cos x + yx) \quad (255)$$

and the Langevin equation (212) describing the dynamics of the Brownian particle becomes

$$\ddot{x}(t) + \beta' \dot{x}(t) + g[\sin x(t) - y]/2 = F(t) \cdot \eta / \sqrt{2mk_B T} \quad (256)$$

where $\beta' = \eta\zeta/m$ is the dimensionless friction parameter, and the white noise force $F(t')$ satisfies

$$\overline{F(t)} = 0, \quad \overline{F(t_1)F(t_2)} = \eta\beta' \delta(t_1 - t_2) \quad (257)$$

Typical examples of physical systems modeled by Brownian motion in a tilted periodic potential and described by the Langevin equation (256) are presented in Table I.

The corresponding Klein–Kramers (Fokker–Planck) equation for the joint PDF $W(x, \dot{x}, t)$ of the phase space variables x and \dot{x} may be written [16]

$$\frac{\partial W}{\partial t} = L_{\text{FP}} W \quad (258)$$

where the Fokker–Planck operator L_{FP} is given in our dimensionless variables by

$$L_{\text{FP}} W = -\dot{x} \frac{\partial W}{\partial x} + \frac{1}{2} \frac{\partial V}{\partial x} \frac{\partial W}{\partial \dot{x}} + \beta' \left(\frac{\partial(\dot{x}W)}{\partial \dot{x}} + \frac{1}{2} \frac{\partial^2 W}{\partial \dot{x}^2} \right) \quad (259)$$

Now the periodic solutions of Eq. (256) or (258) cannot describe escape of the particle from the well because the period 2π of the potential coincides with the domain of the well. Hence, to investigate the escape process across the multiwell potential generated by Eq. (253), one has to obtain a *nonperiodic* or *running* solution of Eq. (256) or (258) [16]. In order to obtain a nonperiodic solution of the Klein–Kramers equation (258), we make the *Ansatz* [16]

$$W(x, \dot{x}, t) = \int_{-1/2}^{1/2} \tilde{W}(k, x, \dot{x}, t) e^{ikx} dk \quad (260)$$

where \tilde{W} is periodic in x with period 2π and it is assumed that k is restricted to the first Brillouin zone, $-1/2 \leq k \leq 1/2$. The periodic function \tilde{W} can then be expanded in a truncated Fourier series in x and in orthogonal Hermite functions in \dot{x} [16]. A similar approach may be used for the solution of the Langevin equation (256).

TABLE I
 Modeled by Brownian Motion in a Tilted Periodic Potential $V(x) = -g(\cos x + yx)$ and Described by the Langevin equation (256)

	Physical Parameters	Dimensionless Magnitude, g	Tilt Parameter, y	Characteristic Time, η	Dimensionless Damping, β'
Brownian motion of a particle in a tilted periodic potential	x : dimensionless coordinate λ : random force m : mass of the particle V_0 : potential magnitude K : constant force ζ : friction coefficient	$\frac{V_0}{k_B T}$	$\frac{aK}{2\pi V_0}$	$\frac{a}{2\pi} \sqrt{\frac{m}{2k_B T}}$	$\frac{\zeta\eta}{m}$
Tunneling junction: capacitively coupled (CSJ) model	x : phase difference λ : noise current I_c : maximum Josephson current I_{dc} : bias dc current e : electron charge \hbar : Planck's constant C : capacitance R : resistance	$\frac{\hbar I_c}{2ek_B T}$	$\frac{I_{dc}}{I_c}$	$\frac{\hbar}{2e} \sqrt{\frac{C}{2k_B T}}$	$\frac{\eta}{RC}$
Brownian motion of a rotor driven by a torque [44]	x : angular coordinate λ : random torque I : moment of inertia V_0 : potential magnitude K : constant torque ζ : friction coefficient	$\frac{V_0}{k_B T}$	$\frac{K}{V_0}$	$\sqrt{\frac{I}{2k_B T}}$	$\frac{\zeta\eta}{I}$

Following [53] we calculate the dynamic structure factor $\tilde{S}(k, \omega)$, which is the Fourier transform over time of the equilibrium translational correlation function $S(k, t) = \langle e^{ik[x(t)-x(0)]} \rangle_0$, where $x(0)$ the initial value of $x(t)$ and the angular brackets denote a stationary averaging. Thus, we introduce the set of stationary correlation functions $c_{n,p}(k, t)$ defined as

$$c_{n,p}(k, t) = \frac{1}{\sqrt{2^n n!}} \langle e^{ik[x(t)-x(0)]} e^{ipx(t)+V[x(t)]/2} H_n[\dot{x}(t)] \rangle_0 \quad (261)$$

Equation (256) now may be recast as a hierarchy of equations for the correlation functions $c_{n,p}(k, t)$, namely [53]

$$\begin{aligned} \frac{d}{dt'} c_{n,p}(k, t) = & -n\beta' c_{n,p}(k, t) \\ & + \sqrt{\frac{n+1}{2}} \left\{ \left[i(p+k) - \frac{gy}{2} \right] c_{n+1,p}(k, t) - \frac{ig}{4} [c_{n+1,p+1}(k, t) - c_{n+1,p-1}(k, t)] \right\} \\ & + \sqrt{\frac{n}{2}} \left\{ \left[i(p+k) + \frac{gy}{2} \right] c_{n-1,p}(k, t) + \frac{ig}{4} [c_{n-1,p+1}(k, t) - c_{n-1,p-1}(k, t)] \right\} \end{aligned} \quad (262)$$

Having determined the $c_{0,p}(k, t)$ from Eq. (262), the function $S(k, t)$ can be evaluated in series form as [16] (see also Section III.C)

$$S(k, t) = \sum_{p=0}^{\infty} a_p c_{0,p}(k, t) = (2\pi)^{-1} Z \sum_{p=0}^{\infty} c_{0,p}^*(k, 0) c_{0,p}(k, t) \quad (263)$$

where the initial conditions $c_{0,p}(k, 0)$ for $c_{0,p}(k, t)$ are given by [16]

$$c_{0,p}(k, 0) = Z^{-1} \int_0^{2\pi} e^{ipx-V(x)/2} dx, \quad Z = \int_0^{2\pi} e^{-V(x)} dx \quad (264)$$

(the asterisk denotes the complex conjugation). Here, we have written

$$\begin{aligned} e^{ikx(t')} &= e^{V[x(t')]/2} \sum_{p=0}^{\infty} a_p e^{i(p+k)x(t')} \\ a_p &= \frac{1}{2\pi} \int_0^{2\pi} dx e^{-ipx-V(x)/2} = \frac{1}{2\pi} Z c_{0,p}^*(k, 0) \end{aligned}$$

Equation (262) (equivalent to that derived by Risken [16] from the Fokker–Planck equation) is the desired recurrence equation for the statistical moments. This equation can be solved by the matrix continued fraction method to yield the one-sided Fourier transform of the dynamic structure factor $\tilde{S}(k, \omega) = \int_0^{\infty} S(k, t) e^{-i\omega t} dt$ (see Appendix B.4). Having determined $\tilde{S}(k, \omega)$, the longest relaxation time τ

and decay rate $\Gamma \approx \tau^{-1}$ can be evaluated as follows. Defining the decay rate $\Gamma \approx \tau^{-1}$ as

$$\tau^{-1} = \int_{-1/2}^{1/2} \tau^{-1}(k) dk \quad (265)$$

where the time $\tau(k)$ is a characteristic time associated with the long-time behavior of the function $S(k, t')$ that can be approximated as $t \rightarrow \infty$ by an exponential $S(k, t') \sim h(k)e^{-t/\tau(k)}$ [50]. In the frequency domain as $\omega \rightarrow 0$, this approximation corresponds to

$$\tilde{S}(k, \omega) = \frac{h(k)}{i\omega + \tau^{-1}(k)} \quad (266)$$

Thus, $\tau^{-1}(k)$ can be extracted as [50]

$$\tau^{-1}(k) = \lim_{\omega \rightarrow 0} i\omega \left[\frac{\tilde{S}(k, 0)}{\tilde{S}(k, \omega)} - 1 \right]^{-1} \quad (267)$$

The dynamic structure factor $\tilde{S}(k, \omega)$ can be calculated exactly by solving the differential–recurrence equation (262) using matrix continued fractions [16] (as described in Appendix B) and may be compared with the characteristic time $\tau(k)$ and the decay rate $\Gamma \approx \tau^{-1}$ evaluated from Eqs. (265) and (267).

2. Turnover Equation

An analytical approximation to the decay rate τ^{-1} in a tilted periodic potential has also been obtained by Mel'nikov [8,9] by again reducing the underdamped Klein–Kramers equation to an integral equation of Wiener–Hopf type. The Mel'nikov expression for the longest relaxation time τ_M is [8,9]

$$\tau_M = \tau_{\text{IHD}}/A(\Delta, gy) \quad (268)$$

where τ_{IHD} is the longest relaxation time in the IHD limit, which is given by the Kramers IHD formula [8,9]

$$\tau_{\text{IHD}} = 4\pi\eta \left(\sqrt{\beta'^2 + 2g} - \beta' \right)^{-1} e^{\Delta V} \quad (269)$$

ΔV is the height of the lowest barrier (see Fig. 18), namely,

$$\Delta V = 2g \left(\sqrt{1 - y^2} + y \arcsin y - \pi y/2 \right) \quad (270)$$

The function A (which now takes into account the periodic nature of the potential) in Eq. (268) is defined as [8,9]

$$A(\Delta, f) = \int_{-1/2}^{1/2} w(k, \Delta, f) dk \quad (271)$$

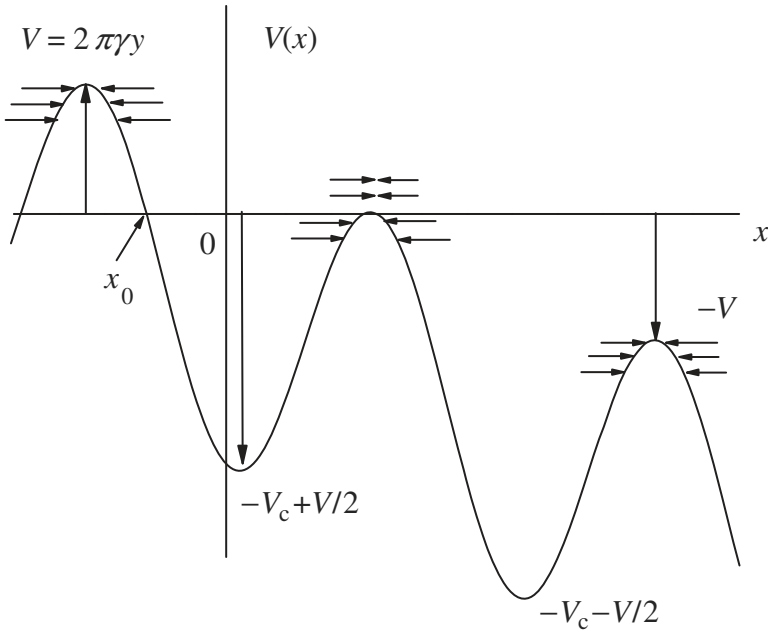


Figure 18. Potential $V(x) = -g(\cos x + yx) + C$ with $C = \pi y - y \arcsin y - (1 - y^2)^{1/2}$, $V = 2\pi g y$, and $V_c = 2g(\sqrt{1 - y^2} + y \arcsin y)$.

where

$$w(k, \Delta, f) = 4 \sin(\pi k) \sin[\pi(k + if)] e^{-\pi f + \Xi(k, \Delta, f) - \Xi(0, 2\Delta, 0)/2} \quad (272)$$

$$\begin{aligned} \Xi(k, \Delta, f) &= \sum_{n=1}^{\infty} n^{-1} \cos[\pi n(2k + if)] \\ &\times \left\{ \operatorname{erfc} \left[\sqrt{n\Delta} \left(\frac{1}{2} + \frac{\pi f}{\Delta} \right) \right] e^{n\pi f} \right. \\ &\left. + \operatorname{erfc} \left[\sqrt{n\Delta} \left(\frac{1}{2} - \frac{\pi f}{\Delta} \right) \right] e^{-n\pi f} \right\} \end{aligned} \quad (273)$$

and $\operatorname{erfc}(x)$ is the complementary error function defined as $\operatorname{erfc}(x) = (2/\sqrt{\pi}) \int_x^{\infty} e^{-t^2} dt$ [72]. (Alternative forms of the function A are given in Ref. [8].) For zero tilt ($y = 0$), Eq. (272) can be simplified to yield [50]

$$w(k, \Delta, 0) = 4 \sin^2(\pi k) e^{\Xi(k, \Delta, 0) - \Xi(0, 2\Delta, 0)/2} \quad (274)$$

where $\Xi(k, \Delta, 0) = 2 \sum_{n=1}^{\infty} n^{-1} \operatorname{erfc}(\sqrt{n\Delta}/2) \cos(2\pi nk)$. The dimensionless Kramers parameter Δ is related to the action associated with the path along the top of the lowest barrier given by

$$\Delta = 2\beta' \int_{x_0}^{-\arcsin y} \sqrt{-V(x)} dx = 2\beta' \sqrt{g} \int_{x_0}^{-\arcsin y} \sqrt{\sqrt{1 - y^2} - \cos x + y(x + \arcsin y)} dx \quad (275)$$

where x_0 is an appropriate solution of the equation $V(x_0) = 0$. On this path, a particle starts with zero velocity at the top of the barrier and, having descended into the well, returns again to the top of the barrier [135]. For small tilt $y \ll 1$, Δ has the following behavior

$$\frac{\Delta}{\delta_0} = 1 - \frac{1}{32} \left\{ \pi \left[9 - 4 \log(\pi y/4) \right] y + \sqrt{\pi} y^{3/2} \right\} + \dots \quad (276)$$

where $\delta_0 = 8\beta' \sqrt{2g}$ is the action for zero tilt. If y approaches 1, Δ can be approximated as [135]

$$\Delta \approx 3\Delta_0 [2(1-y)]^{5/4}/5 \quad (277)$$

The normalized action Δ/δ_0 evaluated from Eqs. (275)–(277) is shown in Fig. 19.

Now $A(\Delta) \rightarrow 1$ as $\Delta \rightarrow \infty$ and $A(\Delta)/\Delta \rightarrow 2$ as $\Delta \rightarrow 0$. Thus, for very high damping, $\beta' \rightarrow \infty$, Eq. (268) yields the VHD asymptote

$$\tau_{\text{VHD}} = 4\pi\eta\beta'g^{-1} e^{\Delta V} \quad (278)$$

In the VLD limit ($\beta' \rightarrow 0$), one has from Eq. (268)

$$\tau_{\text{VLD}} = \frac{\pi\eta}{\beta'\delta\sqrt{g/2}} e^{\Delta V} \quad (279)$$

which is the result of Büttiker and Landauer [135] (in our notation).

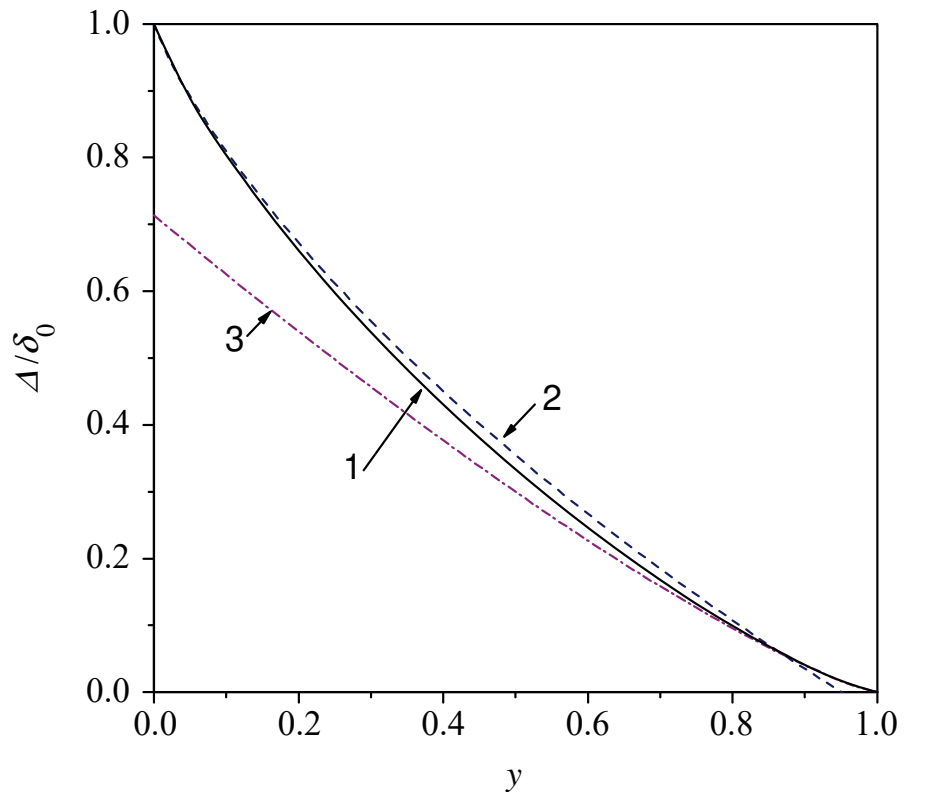


Figure 19. The normalized action Δ/δ_0 versus the tilt parameter y . Solid line: Eq. (275). Dashed line: Eq. (276). Dashed-dotted line: Eq. (277).

The Mel'nikov method (just as other asymptotic methods) is valid in the high-barrier (low-temperature) limit only. In order to accurately estimate τ for a low barrier, one should use alternative methods such as the MFPT [2]. The MFPT may be easily calculated for all systems with dynamics governed by *single* variable Fokker–Planck equations in terms of the equilibrium (stationary) distribution function W_0 and diffusion coefficient $D^{(2)}$ only. The merit of this method is that it again allows us to obtain VHD and VLD solutions, valid for *all barrier heights* including *very low* barriers, where asymptotic methods (like that of Mel'nikov) fail. In the next section, we use the MFPT to evaluate the decay rate τ^{-1} in the VHD and VLD limits at zero tilt $y = 0$. Here, the results can be given in closed form.

3. The Mean First Passage Time Asymptotes for the Decay Rate at Zero Tilt

In the VHD limit ($\beta' \gg 1$), the appropriate single variable Fokker–Planck (Smoluchowski) equation for the PDF $W(x, t)$ is [16]

$$\frac{\partial}{\partial t} W = \frac{1}{2\beta} \left\{ \frac{\partial}{\partial x} (g \sin x W) + \frac{\partial^2}{\partial x^2} W \right\} \quad (280)$$

Since the diffusion coefficient $D^{(2)} = (2\beta')^{-1}$, the longest relaxation time τ can be estimated via the mean first passage time [2] and is thus given by [68]

$$\tau \sim \tau_{\text{VHD}}^{\text{MFPT}} = 2\beta'\eta \int_{-\pi}^{\pi} \frac{1}{W_0(x)} \int_{-\pi}^x W_0(\phi) d\phi dx = 2\beta'\eta \int_{-\pi}^{\pi} \int_{-\pi}^x e^{g(\cos \phi - \cos x)} d\phi dx \quad (281)$$

where the equilibrium Boltzmann distribution function $W_0(x)$ is given by

$$W_0(x) = \frac{e^{g \cos x}}{2\pi I_0(g)} \quad (282)$$

and $I_0(z)$ is the modified Bessel function [72] of the first kind. The time $\tau_{\text{VHD}}^{\text{MFPT}}$ is the time needed for the Brownian particle starting at the top of the barrier $x = -\pi$ to attain, having reached the bottom of a well, the neighboring top at $x = \pi$.

In the opposite low damping limit ($\beta' \ll 1$), in order to obtain a single variable Fokker–Planck equation, we again introduce as variables the energy of the particle

$$\varepsilon = \dot{x}^2 - g \cos x \quad (283)$$

and the time w (phase) measured along a closed trajectory in phase space. These comprise the action–angle variables [2] of the problem. The energy ε varies very slowly with time. Consequently, it is a slow variable in comparison to the phase w . By using the method of Praestgaard and van Kampen [69], that is, averaging

the Fokker–Planck equation (258) over the fast phase variable w , we again have a single variable Fokker–Planck equation for the PDF $W(\varepsilon, t)$ in energy space

$$\frac{\partial W}{\partial t} = 2\beta' \left[\frac{\partial}{\partial \varepsilon} \left(\overline{\dot{x}^2}(\varepsilon) - \frac{1}{2} \right) + \frac{\partial^2}{\partial \varepsilon^2} \overline{\dot{x}^2}(\varepsilon) \right] W \quad (284)$$

where the double overbar denotes averaging over the fast phase variable. Because the diffusion coefficient is

$$D^{(2)} = 2\beta' \overline{\dot{x}^2}(\varepsilon) = 2\beta' [\varepsilon + g \overline{\cos x}(\varepsilon)] \quad (285)$$

the time τ is then given by

$$\tau \sim \tau_{\text{VLD}}^{\text{MFPT}} = \frac{\eta}{2\beta'} \int_{-g}^g \frac{1}{[\varepsilon + g \overline{\cos x}(\varepsilon)] W_0(\varepsilon)} \int_{-g}^{\varepsilon} W_0(x) dx d\varepsilon \quad (286)$$

The calculation of $W_0(\varepsilon)$ and the integrals in Eq. (286) is described in Appendix C.4. The ranges of applicability of the VHD and VLD MFPTS [Eqs. (281) and (286)] are the same as those of the corresponding Fokker–Planck equations (280) and (284), namely, the VHD and VLD limits, respectively. In practice, Eqs. (281) and (286) may be used for $\beta' > 5$ and $\beta' < 0.01$.

4. Asymptotic Formula and Matrix Solution: Comparison of the Results

The longest relaxation time predicted by the turnover formula, Eq. (268), and the inverse decay rate calculated numerically by matrix continued fraction methods are shown in Figs. 20 and 21 as functions of β' for different values of the barrier height and tilt parameters. Here, the IHD [Eq. (269)], VHD [Eq. (278)], and VLD [Eq. (279)] asymptotes for τ are also shown for comparison. Apparently in the high-barrier limit Eq. (268) provides a good approximation to the decay rate for all values of the friction parameter β' including the VHD, VLD, and the Kramers turnover regions. The quantitative agreement in damping behavior may be explained as follows. The behavior of the escape rate as a function of the barrier height parameter g for large g is as before approximately Arrhenius-like and arises from an *equilibrium* property of the system (namely the Boltzmann distribution at the bottom of the well). In contrast, the damping dependence of the escape rate is due to *nonequilibrium* (dynamical) properties of the system and so is contained in the prefactor A only, the detailed nature of which depends on the behavior of the energy distribution function at the barrier points [74]. The Mel'nikov–Meshkov approach [12,78] yields the distribution function at the barrier point for all values of the damping allowing one to evaluate the damping dependence of the prefactor $\mu \sim A$ in Eq. (19).

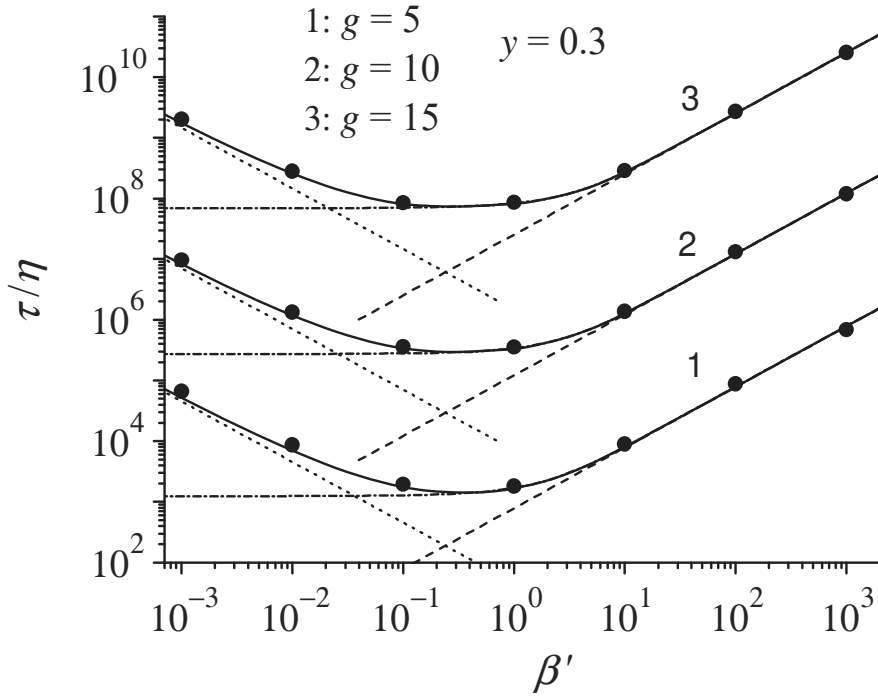


Figure 20. The longest relaxation time τ/η versus the friction parameter β' for a tilt parameter $y=0.3$ and different values of the barrier parameter $g=5, 10,$ and 15 . Solid line: the Mel'nikov Eq. (268); dashed line: the VHD Eq. (278); dashed-dotted line: the IHD Eq. (269); dotted line: the VLD Eq. (279); filled circles: exact numerical solution, Eq. (265).

In spite of very good overall agreement between numerical results and the universal equation (268), a marked difference (on the order of 10–40%) between numerical and analytical results exists in the VLD region at moderate barriers (this difference decreases with increasing g , see Fig. 20) Such a difference has already been noted for other systems (see, e.g., Refs [47,49]). Thus, in order to improve the accuracy of the turnover formula, Mel'nikov [74] suggested a systematic way of accounting for finite-barrier corrections. Analysis of the translational Brownian motion in a periodic cosine potential has demonstrated [51] that if such corrections are included, the accuracy of the turnover formula is considerably improved for

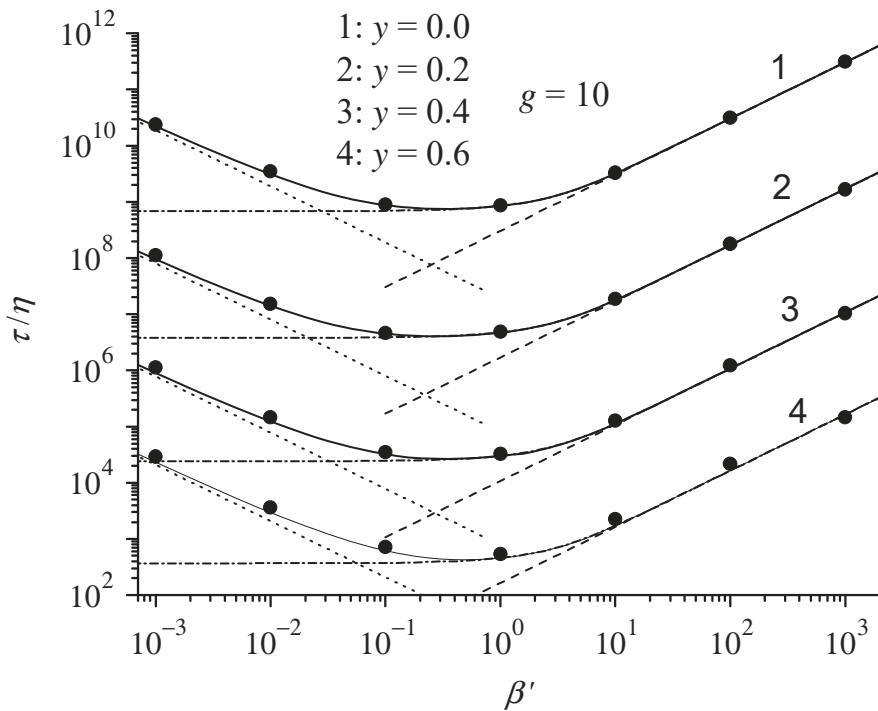


Figure 21. τ/η versus the friction parameter β' for the barrier parameter $g=10$ and different values of the tilt parameter $y=0.0, 0.2, 0.4,$ and 0.6 . Solid line: the Mel'nikov equation (268); dashed line: the VHD Eq. (278); the IHD Eq. (269); dotted line: the VLD Eq. (279); filled circles: exact solution, Eq. (265).

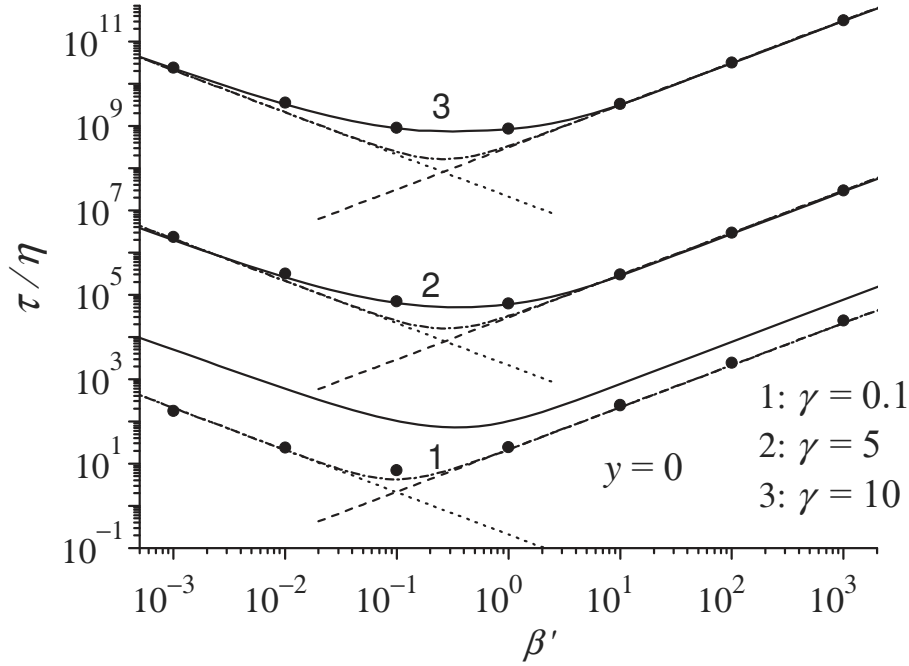


Figure 22. τ/η versus β' for the tilt parameter $y=0$ and $g=0.1, 5,$ and 10 . Solid line: the Mel'nikov equation (268); dashed line: the VHD MFPT Eq. (281); dotted line: the VLD MFPT Eq. (286); dashed-dotted line: the *ad hoc* extrapolating Eq. (287); filled circles: exact solution, Eq. (265).

Brownian motion in a periodic potential with zero tilt, that is, $y=0$. One would expect a similar improvement for nonzero tilt.

For zero tilt, $y=0$, the longest relaxation time τ predicted by the turnover equation (268) and the inverse decay rate calculated numerically by matrix continued fraction methods are shown in Figs. 22 as functions of β' for various barrier heights including the very low barrier $g=0.1$. Here, the VHD [Eq. (281)] and VLD [Eq. (286)] asymptotes for τ calculated from the MFPT are also shown for comparison. In the VHD and VLD limits, these asymptotes may be used to estimate τ for all barrier heights. For small barriers $g=0.1$, the turnover formula is obviously invalid. However, for small barriers the simple *ad hoc* extrapolating equation [2]

$$\tau \sim \tau_{\text{VHD}}^{\text{MFPT}} + \tau_{\text{VLD}}^{\text{MFPT}} \quad (287)$$

provides a satisfactory estimate of the longest relaxation time τ for all damping.

The real and imaginary parts of the normalized dynamic structure factor $\tilde{S}(k, \omega)/\tilde{S}(k, 0)$, for various values of the tilt parameter y are shown in Fig. 23 with barrier parameter $g=10$, the friction coefficient is $\beta'=10$, and $k=0.2$. For comparison, we also show in these figures the pure Lorentzian spectra

$$\frac{\tilde{S}_L(k, \omega)}{\tilde{S}(k, 0)} = \frac{1}{1 + i\omega\tau_k} \quad (288)$$

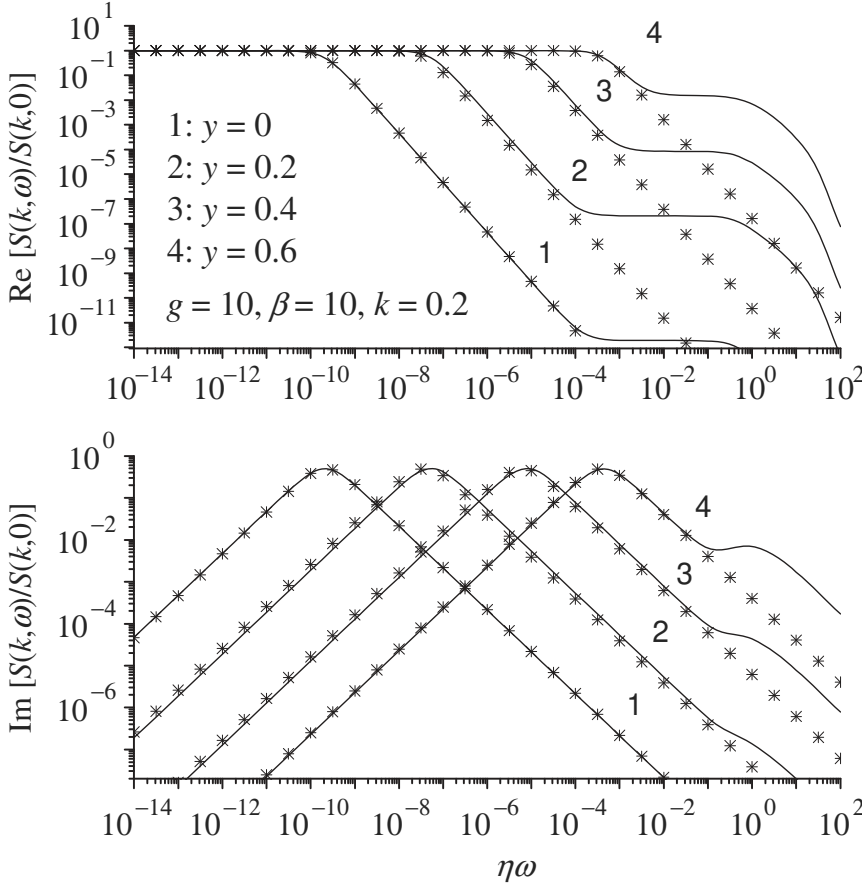


Figure 23. The real and imaginary parts of the normalized dynamic structure factor $\tilde{S}(k, \omega)/\tilde{S}(k, 0)$ versus $\omega\eta$ for various values of the tilt parameter y and for the barrier parameter $g = 10$, the friction coefficient $\beta' = 10$ and $k = 0.2$. Solid lines: numerical calculation. Asterisks: Eq. (288).

where the relaxation time $\tau_k = 1/\text{Re}[\tau_M^{-1}(k)]$ is related to the τ_M from the universal equation (268) via $\tau_M^{-1} = 2\int_0^{1/2}\text{Re}[\tau_M^{-1}(k)]dk$. Apparently, the simple Lorentzian equation (288) describes perfectly the low-frequency part of the dynamic structure factor $\tilde{S}(k, \omega)/\tilde{S}(k, 0)$.

Thus, we have demonstrated how the matrix continued fraction method of solution of nonlinear Langevin equations [14] may be successfully applied to a Brownian particle moving in the tilted periodic potential, Eq. (253) for wide ranges of the barrier parameter g , tilt parameter y , and the damping parameter β' . We have shown that in the low-temperature limit, the Mel'nikov formula for the longest relaxation time, Eq. (268), yields satisfactory agreement with the numerical results for all values of damping. In practical calculations, Eq. (268) may be used for $g \geq 1$, 5 and $0.8 \geq y \geq 0$. For $1.0 \geq y > 0.8$ (where a parabolic approximation of the barrier top is no longer valid), the matrix continued fraction solution must be used. For small g (where asymptotic methods like that of Mel'nikov are not applicable) and $y = 0$, Eqs. (281), (286), and (287) yield a good estimate for the longest relaxation time. Moreover, the Mel'nikov equation (268) allows one to accurately estimate the damping dependence of the low-frequency parts of the dynamic structure factor $\tilde{S}(k, \omega)$ via the simple approximate analytical formula, Eq. (288).

We have shown that the turnover formula for evaluating the longest relaxation time τ as a function of the dissipation parameter for Brownian particles in a tilted periodic potential provides in the low-temperature limit excellent agreement with

the exact continued fraction solution for all values of the dissipation parameter including the VLD, VHD, and turnover regions. A similar conclusion may be drawn [48,57,58,60,64,136] for diverse stochastic systems modeled by Brownian motion in multiwell potentials with equivalent and nonequivalent wells, where the validity of the turnover equation for $\tau \sim \Gamma^{-1}$ (Γ is the escape rate) has been verified by comparison with numerical solutions of the governing Langevin or Fokker–Planck equations. Thus, the turnover equation for the escape rate appears to yield an effective and powerful tool for evaluating the damping dependence of the prefactor A for a wide class of nonlinear stochastic systems even in the tilted cosine potential problem where the stationary solution differs from the Maxwell–Boltzmann distribution. It is obvious that the description of the relaxation processes in terms of either the Fokker–Planck or Langevin equations neglects quantum effects. These effects become important at very low temperatures and necessitate an appropriate quantum mechanical treatment so that Mel’nikov [8,9] and Rips and Pollak [78] have extended the turnover formula for mechanical particles to account for quantum tunneling in a semiclassical way. We have seen that the classical turnover formula for the escape rate may be confirmed as an accurate approximation to the exact escape rate of a mechanical Brownian particle because one may exactly solve the corresponding Fokker–Planck equation describing the evolution of the distribution function in phase space using matrix continued fractions. In order to verify formulas for the escape rate that incorporate quantum effects, it is necessary to identify the appropriate quantum mechanical master equation [137,138] underlying the relaxation process, which becomes the Fokker–Planck equation in the classical limit. A promising candidate seems to be the Caldeira–Leggett [80] quantum master equation for the time evolution of the Wigner transform of the reduced density operator (here the relationship between the quantum density operator and the semiclassical distribution function is given by the Wigner transformation [139]). The Caldeira–Leggett approach may be used for all values of damping. In the VHD limit, one can use the quantum Smoluchowski equation, which to leading order coincides in form with the classical Smoluchowski equation, nevertheless containing essential quantum corrections [140–142]. Such an approach to the quantum mechanical problem also lends itself to solution by the continued fraction methods we have described [137,138] so that the turnover quantum escape rate equations can be tested in a similar manner to that which we have described here, a subject that will occupy the final part of our chapter.

H. Escape Rate Formulas for Superparamagnets

The application of Kramers’ escape theory to superparamagnetic relaxation in the IHD limit has been given in detail by Smith and de Rozario [143], Brown [144], Klik and Gunther [145], and Geoghegan et al. [37] (all this work is described in Ref. [3]). Klik and Gunther [145] used Langer’s method (described in

Section II.A.5) and realized that the various Kramers damping regimes also applied to magnetic relaxation of single-domain ferromagnetic particles.

The starting point of Brown's treatment of the dynamical behavior of the magnetization \mathbf{M} for a single-domain particle is Gilbert's equation [146], which without thermal agitation is

$$\dot{\mathbf{M}} = \gamma \mathbf{M} \times (\mathbf{H} - \eta \dot{\mathbf{M}}) \quad (289)$$

In Eq. (289), γ is the gyromagnetic ratio, η is a phenomenological damping constant,

$$\mathbf{H} = -\frac{\partial V}{\partial \mathbf{M}} = -\left(\mathbf{i} \frac{\partial V}{\partial M_X} + \mathbf{j} \frac{\partial V}{\partial M_Y} + \mathbf{k} \frac{\partial V}{\partial M_Z} \right) \quad (290)$$

and V is the Gibbs free energy density (the total free energy is vV , v is the volume of the particle). In general, \mathbf{H} represents the *conservative* part and $\eta \dot{\mathbf{M}}$ the *dissipative* part of an "effective field." Brown now supposes that in the presence of thermal agitation, the dissipative "effective field" $-\eta \dot{\mathbf{M}}$ describes only the statistical average of the rapidly fluctuating random forces due to thermal agitation, and that for an individual particle, this term must become $-\eta \dot{\mathbf{M}} + \mathbf{h}(t)$, where the Gaussian white noise random field $\mathbf{h}(t)$ has the properties

$$\overline{h_i(t)} = 0, \quad \overline{h_i(t_1)h_j(t_2)} = (2k_B T \eta / v) \delta_{ij} \delta(t_2 - t_1) \quad (291)$$

Here, the indices $i, j = 1, 2, 3$ correspond to the Cartesian axes X, Y, Z of the laboratory coordinate system. The overbars denote the statistical averages over a large number of moments, which have all started with the same orientation (ϑ, φ) (here we use spherical polar coordinates, see Fig. 24). On assuming that the $h_i(t)$ obey Isserlis's theorem [14], Brown was then able to derive after a long and tedious calculation using the methods of Wang and Uhlenbeck [146–148], the Fokker–Planck equation for the density of magnetization orientations $W(\vartheta, \varphi, t)$ on a sphere of constant radius M_S . This procedure may be circumvented, however, using an alternative approach given by Brown [146].

In order to illustrate this, we first write (by cross multiplying vectorially by \mathbf{M} and using the triple vector product formula) Gilbert's equation in the absence of thermal agitation (noiseless equation) as an explicit equation for $\dot{\mathbf{M}}$, namely,

$$\dot{\mathbf{M}} = \alpha^{-1} h' M_S (\mathbf{M} \times \mathbf{H}) + h' (\mathbf{M} \times \mathbf{H}) \times \mathbf{M} \quad (292)$$

where $\alpha = \gamma \eta M_S$ is a dimensionless damping coefficient and

$$h' = \frac{\alpha \gamma}{(1 + \alpha^2) M_S} \quad (293)$$

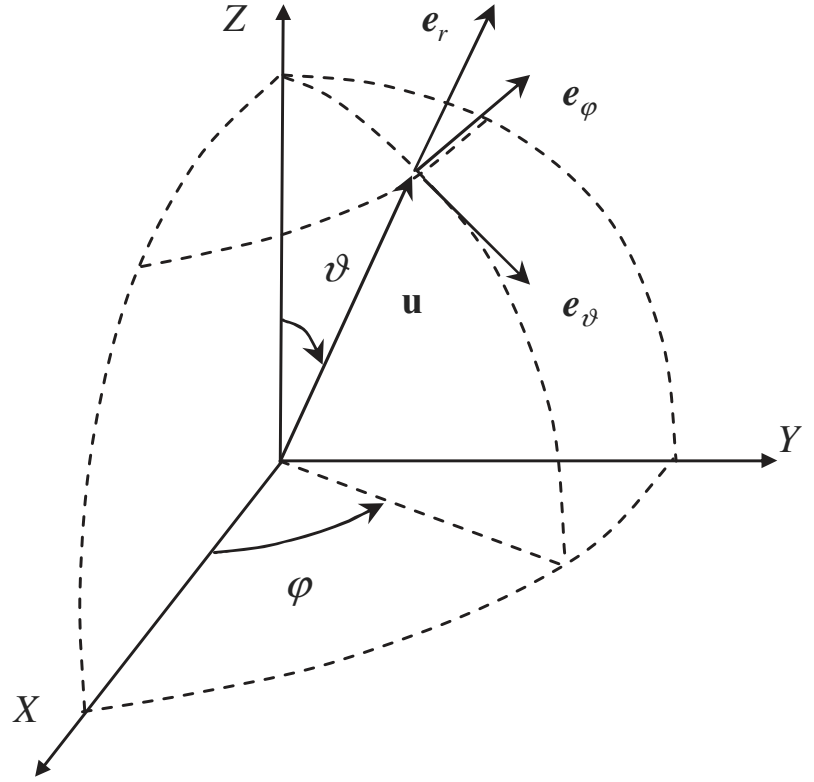


Figure 24. Spherical polar coordinate system.

Equation (293) has the mathematical form of the earlier Landau–Lifshitz equation, where precessional and alignment terms are distinguished namely,

$$\dot{\mathbf{M}} = \gamma(\mathbf{M} \times \mathbf{H}) + \frac{\alpha\gamma}{M_S}(\mathbf{M} \times \mathbf{H}) \times \mathbf{M} \quad (294)$$

which may be written from Eq. (293) by taking the low damping limit, $\alpha \ll 1$ (usually, α lies in the range 0.01–1). On writing $\mathbf{M} = \mathbf{u}M_S$, Eq. (293) becomes

$$\dot{\mathbf{u}} = -\frac{h'}{\alpha} \left(\mathbf{u} \times \frac{\partial V}{\partial \mathbf{u}} \right) + h' \mathbf{u} \times \left(\mathbf{u} \times \frac{\partial V}{\partial \mathbf{u}} \right) \quad (295)$$

Here instead of \mathbf{M} we use the unit vector \mathbf{u} , where the Cartesian coordinates are the direction cosines u_i of \mathbf{M} so that $\partial/\partial \mathbf{M}$ may be replaced by $M_S^{-1} \partial/\partial \mathbf{u}$, where $\partial/\partial \mathbf{u}$ means the gradient on the surface of the unit sphere [146] so that in the spherical coordinate system (Fig. 24), the operator $\partial/\partial \mathbf{u}$ is

$$\frac{\partial}{\partial \mathbf{u}} = \frac{\partial}{\partial \vartheta} \mathbf{e}_\vartheta + \frac{1}{\sin \vartheta} \frac{\partial}{\partial \varphi} \mathbf{e}_\varphi \quad (296)$$

We show in detail how Langer’s method may be used in superparamagnetic relaxation. Again, we deal with an energy (or Hamiltonian) function, $E = V(\vartheta, \varphi)$, with minima at points A and B separated by a barrier (saddle point) at C , see Fig. 1. We use spherical polar coordinates (ϑ, φ) , where ϑ is the polar angle and φ is the

azimuthal angle as usual. The noiseless Gilbert equation (295) takes the form in the coordinates $(p = \cos \vartheta, \varphi)$ [144]

$$\dot{p} = -h'(1 - p^2)V_p - h'\alpha^{-1}V_\varphi, \quad \dot{\varphi} = h'\alpha^{-1}V_p - h'(1 - p^2)V_\varphi \quad (297)$$

where subscripts denote the partial derivatives. We linearize these equations about the saddle point and determine λ_+ from the transition matrix as in the Klein–Kramers case of Section II.A.5. Thus, expanding the Hamiltonian $V(p, \varphi)$ as a Taylor series about the saddle point $(p_C = \cos \vartheta_C, \varphi_C)$, we obtain

$$V = V_0 + \frac{1}{2} \left[V_{pp}^{(0)}(p - p_C)^2 + 2V_{p\varphi}^{(0)}(p - p_C)(\varphi - \varphi_C) + V_{\varphi\varphi}^{(0)}(\varphi - \varphi_C)^2 \right] \quad (298)$$

where the superscript denotes the value of the relevant function at the saddle point. We remark, following Klik and Gunther [145], that the Hamiltonian is defined on a phase space that is a closed manifold [the space (ϑ, φ) is the surface of a unit sphere] and thus a local energy minimum is surrounded by two or more saddle points, depending on the symmetry of the problem. The total probability flux out of the metastable minimum equals the sum of the fluxes through all the saddle points. In asymmetrical cases, for example, when an external field is applied, some of these fluxes become exponentially small and may safely be neglected. The total flux out of the metastable minimum is then dominated by the energetically most favorable path. Now, if the coordinates of the saddle point are (p_C, φ_C) , we have

$$\frac{\partial V}{\partial p} = (p - p_C)V_{pp}^{(0)} + (\varphi - \varphi_C)V_{p\varphi}^{(0)}, \quad \frac{\partial V}{\partial \varphi} = (p - p_C)V_{p\varphi}^{(0)} + (\varphi - \varphi_C)V_{\varphi\varphi}^{(0)} \quad (299)$$

Now, let the saddle point C of interest lie on the equator $p = 0$ and make the transformation $\varphi - \varphi_C \rightarrow \varphi$. Equations (297) then yield

$$\dot{\varphi} = h'\alpha^{-1} \frac{\partial V}{\partial p} - h' \frac{\partial V}{\partial \varphi}, \quad \dot{p} = -h' \frac{\partial V}{\partial p} - h'\alpha^{-1} \frac{\partial V}{\partial \varphi} \quad (300)$$

Thus, the noiseless equation of motion in terms of the state variables is

$$\begin{pmatrix} \dot{\varphi} \\ \dot{p} \end{pmatrix} = h' \begin{pmatrix} -1 & \alpha^{-1} \\ -\alpha^{-1} & -1 \end{pmatrix} \begin{pmatrix} \partial V / \partial \varphi \\ \partial V / \partial p \end{pmatrix} \quad (301)$$

Thus, the linearized Eq. (301) has the form of the canonical Eqs. (31) and so Langer's equation (58) may be used to calculate the IHD escape rate. In particular,

the transport matrix \mathbf{M} and the matrix $\tilde{\mathbf{M}}$ (see Section II.A.4) are given by

$$\mathbf{M} = h' \begin{pmatrix} 1 & -\alpha^{-1} \\ \alpha^{-1} & 1 \end{pmatrix}, \quad \tilde{\mathbf{M}} = h' \begin{pmatrix} -1 & \alpha^{-1} \\ -\alpha^{-1} & -1 \end{pmatrix} \quad (302)$$

Now, the equations of motion (297) linearized at the saddle point become [145]

$$\dot{\varphi} = h' \alpha^{-1} \left[V_{pp}^{(0)} p + V_{p\varphi}^{(0)} \varphi \right] - h' \left[V_{p\varphi}^{(0)} p + V_{\varphi\varphi}^{(0)} \varphi \right] \quad (303)$$

$$\dot{p} = -h' \left[V_{pp}^{(0)} p + V_{p\varphi}^{(0)} \varphi \right] - h' \alpha^{-1} \left[V_{p\varphi}^{(0)} p + V_{\varphi\varphi}^{(0)} \varphi \right] \quad (304)$$

or, in matrix notation,

$$\begin{pmatrix} \dot{\varphi} \\ \dot{p} \end{pmatrix} = h' \begin{pmatrix} \alpha^{-1} V_{p\varphi}^{(0)} - V_{\varphi\varphi}^{(0)} & \alpha^{-1} V_{pp}^{(0)} - V_{p\varphi}^{(0)} \\ -V_{p\varphi}^{(0)} - \alpha^{-1} V_{\varphi\varphi}^{(0)} & -V_{pp}^{(0)} - \alpha^{-1} V_{p\varphi}^{(0)} \end{pmatrix} \begin{pmatrix} \varphi \\ p \end{pmatrix} \quad (305)$$

[the superscript (0) denoting evaluation at the saddle point]. Equations (303) and (304) are the noiseless Langevin equations linearized at the saddle point given by Klik and Gunther [[145], Eq. (3.2)]. The secular equation of Eq. (305) then yields (as in Section II.A.4, 5)

$$\lambda_{\pm} = \frac{h'}{2} \left\{ -[V_{pp}^{(0)} + V_{\varphi\varphi}^{(0)}] \pm \sqrt{[V_{pp}^{(0)} + V_{\varphi\varphi}^{(0)}]^2 - 4(1 + \alpha^{-2})[V_{pp}^{(0)} V_{\varphi\varphi}^{(0)} - (V_{p\varphi}^{(0)})^2]} \right\} \quad (306)$$

The Hessian matrix of the system is

$$\begin{pmatrix} V_{\varphi\varphi} & V_{p\varphi} \\ V_{p\varphi} & V_{pp} \end{pmatrix} \quad (307)$$

and the Hessian itself is *negative* at the saddle point, thus, to ensure a growing disturbance at the saddle point, we must again take the positive sign in Eq. (306). The square of the well angular frequency is [the superscript (*i*) denoting evaluation at the minimum of well *i*]

$$\omega_i^2 = (\gamma/M_S)^2 \left[V_{pp}^{(i)} V_{\varphi\varphi}^{(i)} - (V_{p\varphi}^{(i)})^2 \right] \quad (308)$$

while the squared saddle angular frequency is

$$\omega_0^2 = (\gamma/M_S)^2 \left[V_{pp}^{(0)} V_{\varphi\varphi}^{(0)} - (V_{p\varphi}^{(0)})^2 \right] \quad (309)$$

which, with Langer's equation (58), leads to the Klik and Gunther result for the escape rate [145]

$$\Gamma_i = \frac{\lambda_+ \omega_i}{2\pi\omega_0} e^{-\Delta V_i} \quad (310)$$

where $\Delta V_i = v(V_0 - V_i)/(k_B T)$.

This formula demonstrates the wide-ranging uses of Langer's method and shows clearly how, once the potential landscape is known, all quantities relating to the IHD escape rate may be calculated. We now choose a system of local coordinates, (φ, p) , in the vicinity of the saddle point, where $V_{p\varphi} = 0$. Then we obtain a more compact expression for λ_+ , namely,

$$\lambda_+ \equiv \frac{h'}{2} \left\{ -[V_{pp}^{(0)} + V_{\varphi\varphi}^{(0)}] + \sqrt{[V_{pp}^{(0)} - V_{\varphi\varphi}^{(0)}]^2 - 4\alpha^{-2} V_{pp}^{(0)} V_{\varphi\varphi}^{(0)}} \right\} \quad (311)$$

where we observe that the α^{-2} term represents the effect of the precessional term in the Gilbert equation on the longitudinal relaxation. This *mode coupling effect* is always present in a nonaxially symmetrical potential as the smallest eigenvalue of the Fokker–Planck equation will always *intrinsically* depend on the damping unlike in axial symmetry where the damping only enters via the free diffusion time.

Equations (310) and (311) were also derived from first principles directly using the Kramers escape rate theory without recourse to Langer's work by Smith and de Rozario [143] and Brown [144] and have been reviewed by Geoghegan et al. [37]. In Brown's calculation [144], the free energy density is diagonalized so that in the vicinity of the saddle point and minimum, respectively, we have [37]

$$V = V_0 + [c_1^{(0)}\varphi^2 + c_2^{(0)}p^2] / 2 \quad \text{and} \quad V = V_i + [c_1^{(i)}\varphi^2 + c_2^{(i)}p^2] / 2,$$

where $c_1^{(0)}$ and $c_2^{(0)}$ are the coefficients of the second-order term of the Taylor series of the expansion of V at the saddle point and $c_1^{(i)}$ and $c_2^{(i)}$ are the coefficients of the second-order term in the Taylor series expansion of the energy in the well. Thus, Brown's IHD result for the escape rate [144] reads [cf. Eq. (5.60) of Geoghegan et al. [37], where a detailed derivation is given]

$$\Gamma_i = \frac{\Omega_0 \omega_i}{2\pi\omega_0} e^{-\Delta V_i} \quad (312)$$

where

$$\Omega_0 = \frac{h'}{2} \left[-c_1^{(0)} - c_2^{(0)} + \sqrt{(c_2^{(0)} - c_1^{(0)})^2 - 4\alpha^{-2} c_1^{(0)} c_2^{(0)}} \right]$$

is the damped saddle angular frequency. Obviously Brown's equation (312) coincides with Eq. (310).

We remark that the magnetization reversal time problem differs fundamentally from that of point particles because (i) the magnetic system has two degrees of freedom, the polar ϑ and azimuthal φ angles, (ii) the undamped equation of motion of the magnetization of a single-domain ferromagnetic particle is the gyromagnetic equation, (iii) the Hamiltonian is nonseparable, and (iv) the inertial effects play no role. Notwithstanding, the role of inertia in the mechanical system is essentially mimicked in the magnetic system for nonaxially symmetrical potentials by the gyromagnetic term causing *coupling* or *entanglement* of the transverse and longitudinal modes. Hence, in order to derive escape rate formulas for superparamagnetic particles equivalent to those for mechanical particles, one has to consider in Brown's Fokker–Planck equation a *nonaxially* symmetrical free energy density $V(\vartheta, \varphi)$, where explicit coupling between the two degrees of freedom exists. Thus, both regimes of damping (IHD and VLD) can now occur reflecting the fact that the dynamics of the transverse response affect the dynamics of the longitudinal response and vice versa. This was first realized in 1990 by Klik and Gunther [145]. They showed that the various Kramers damping regimes also apply to magnetic relaxation of single-domain ferromagnetic particles and derived the corresponding VLD formula. Furthermore, they also realized that the magnetic IHD calculations [143,144] are, as described above a special case of Langer's general treatment of the decay of metastable states of systems with many degrees of freedom [13]. Thus, they could understand why Eq. (312) derived for a *nonseparable* Hamiltonian, which is the free energy, applies like the *separable* Hamiltonian result Eq. (20) when the energy loss per cycle of the almost periodic noise-perturbed motion at the saddle point energy $\alpha S_i \gg 1$. If $\alpha S_i \ll 1$, then one may prove using first passage times (details in [3]) that for the escape from a single well

$$\Gamma_i = \Gamma_i^{\text{VLD}} \sim \frac{\alpha S_i \omega_i}{2\pi} e^{-\Delta V_i} \quad (313)$$

where

$$S_i = \frac{v}{k_B T} \oint_{E_C} \left[(1 - p^2) \frac{\partial V}{\partial p} d\varphi - \frac{1}{1 - p^2} \frac{\partial V}{\partial \varphi} dp \right] \quad (314)$$

is the dimensionless action. Equation (313) is effectively the same as the corresponding Kramers result for point particles, Eq. (22). The conditions of applicability of the IHD and VLD solutions for superparamagnets are defined by $\alpha \geq 1$ and $\alpha \ll 1$, respectively.

In the turnover region, $0.01 < \alpha < 1$, Coffey et al. [3,64] have shown that the Mel'nikov–Meshkov formalism connecting the VLD and IHD Kramers escape rates as a function of the dissipation parameter for mechanical particles,

can be extended to include magnetization relaxation of single-domain ferromagnetic particles having nonaxially symmetrical potentials of the magnetocrystalline anisotropy. The turnover equation bridging the VLD and IHD escape rates is given by [3,64]

$$\Gamma_i = A(\alpha S_i) \Gamma_i^{\text{IHD}} \quad (315)$$

where $A(\Delta)$ is the depopulation factor, Eq. (119), which interpolates between the VLD and ID regimes. One may show that Eq. (315) reduces in the IHD and VLD limits to Eqs. (312) and (313), respectively.

We remark that Eqs. (312), (313), and (315) may be used to verify experimentally the Kramers theory for magnetic particles. This has been accomplished using the sophisticated single-particle measurement techniques developed by Wernsdorfer [26]. We further remark that a second interpolation problem arises in the magnetic version of the Kramers escape rate, namely, how to join axially symmetrical and nonaxially symmetrical asymptotic expressions for the longest relaxation time in the limit of small departures from axial symmetry. This problem has been described in detail in Refs [3,149]. Thus, we emphasize that in the derivation of all these formulas it is assumed that the potential is nonaxially symmetrical. If the departures from axial symmetry become small the nonaxially symmetric asymptotic formulas for the escape rate may be smoothly connected to the axially symmetric ones by means of suitable interpolation integrals [3].

Two other important effects occur in bistable potentials. These are (i) the effect of a uniform bias force on the relaxation time and (ii) the stochastic resonance phenomenon. The formulas developed in this section may also be applied to ferrofluids.

III. QUANTUM BROWNIAN MOTION IN A POTENTIAL

A. Escape Rate for Quantum Brownian Motion

1. Escape Rate in the IHD Region

Following Mel'nikov [8], we recall that in the classical regime one starts with the Langevin equation or the corresponding Fokker–Planck equation. However, in the quantum regime one must start by specifying the Hamiltonian of the problem. Now we wish to study the decay rate for particles that experience viscous friction in the classical regime. This condition is insufficient to define the system consisting of particle and heat bath in a unique way. Nevertheless, it is still enough to uniquely determine the effective action of the particle obtained by integration over the variables describing the bath. According to Mel'nikov [8], this conclusion is very important because all models of the heat bath are then equivalent as far as the results for the escape rate are concerned *provided they reproduce the*

same Langevin equation in the classical limit. Mel'nikov [8] considered two different models of the heat bath. In the underdamped regime he accounted for the interaction of a particle with the bath by adding a term describing the effects of the Johnston–Nyquist noise due to the bath to the Hamiltonian of the particle. In contrast in the overdamped regime he assumed that the effect of the bath is mimicked by a string (transmission line) coupled to the particle and tightened in a direction perpendicular to the direction of motion of the particle. Ultimately these procedures lead via a quantum depopulation factor to a high-temperature quantum escape rate valid for all values of the dissipation in the same *ad hoc* manner as the classical case.

We reiterate that in considering the classical case Kramers [15] effectively proceeded using what are essentially two separate theories. In energy-controlled diffusion it is assumed that the dynamics of the particle are almost Newtonian because of the very weak coupling to the bath and the noisy motion is then treated simply as a small perturbation of the noiseless undamped librational motion at the barrier energy governed by Newton's equation. On the other hand, in the IHD or spatially controlled diffusion limit the problem is treated by approximating the potential in the vicinity of the well and saddle by a (hyper) paraboloid and inverted (hyper) paraboloid, respectively. The corresponding linearized multidimensional Fokker–Planck equation is then solved in the vicinity of the barrier in the manner described above. The two approaches are then combined as in the classical Meshkov–Mel'nikov approach via a depopulation factor to yield a formula for the escape rate valid for all values of the dissipative coupling to the bath.

However, as we have mentioned the first systematic (i.e., without *ad hoc* assumptions) solution of the classical Kramers turnover problem was given by Grabert [29] and Pollak et al. [12]. This solution was based on two observations. The first being that escape does not occur along the original system coordinate but along the unstable normal mode of the combined system and bath [2]. The second was a systematic perturbative treatment [29] of the nonlinear part of the potential that couples the unstable mode with the bath of stable modes. This treatment was extended by Rips and Pollak [78] to provide a consistent solution of the quantum Kramers turnover problem. Their method represents a synthesis of the treatment of the well and barrier dynamics of Mel'nikov [8] and Larkin and Ovchinnikov [11] and the normal mode approach to the classical Kramers turnover problem of Pollak et al. In reviewing and simplifying the work of Mel'nikov we shall first give the derivation of the IHD quantum rate in the transparent manner proposed by Pollak [18], as this constitutes the most transparent method of attack on the problem that was originally solved by Wolynes [150] in 1981 using path integrals. Pollak [18] started from the equivalence of the generalized Langevin equation for a Brownian particle to the equation of motion of a particle moving in a potential and bilinearly coupled to a bath of harmonic oscillators. This procedure (which demonstrates using normal mode analysis that classically the IHD Kramers rate is equivalent

to a harmonic multidimensional TST rate) may be extended to the quantum case by quantizing the system plus bath Hamiltonian consisting at the transition state of an assembly of real oscillators and one with imaginary frequency of oscillation representing the unstable barrier-crossing mode. It leads to the result of Wolynes without using path integrals. Alternative calculations [3] based on extensions of Langer's imaginary part of the free energy method to include quantum effects also yield that result. The string-particle model in its essentials goes back to Lamb's (1900) attempt to explain radiation damping in classical electrodynamics [20].

In this section, we use the notation of Pollak's paper [18], namely, q is a coordinate, $V(q)$ is the potential, $V^\#$ is barrier height, and $\eta(t)$ is a time-dependent friction related to the zero-mean Gaussian random force $F(t)$ by the fluctuation–dissipation relation, that is,

$$\langle F(0) F(t) \rangle = k_B T \eta(t) \quad (316)$$

The generalized Langevin equation (for the classical particle) is Eq. (126), namely,

$$M\ddot{q} + \int_0^t \eta(t-t') \dot{q}(t') dt' + \frac{\partial V}{\partial q} = F(t) \quad (317)$$

This equation may be derived from a Hamiltonian with a harmonic oscillator bath [151], that is,

$$H = \frac{p_q^2}{2M} + V(q) + \sum_{j=1}^N \left[\frac{p_j^2}{2m_j} + \frac{1}{2} m_j \left(\omega_j x_j + \frac{C_j}{m_j \omega_j} q \right)^2 \right] \quad (318)$$

(See also [152].) Here, (p_j, x_j) are the momenta and coordinates of the j th bath oscillator whose mass and frequency are m_j and ω_j , respectively. C_j couples the j th bath oscillator to the system. By assuming that at time $t=0$, the bath is in thermal equilibrium, it can be shown [151] that $q(t)$ is governed by Eq. (317) [and Eq. (316)], where the time-dependent friction $\eta(t)$ is

$$\eta(t) = \sum_{j=1}^N \frac{C_j^2}{m_j \omega_j^2} \cos \omega_j t \quad (319)$$

The spectral density of the bath $J(\omega)$ is defined as [152]

$$J(\omega) \equiv \frac{\pi}{2} \sum_{j=1}^N \frac{C_j^2}{m_j \omega_j} \delta(\omega - \omega_j) \quad (320)$$

Hence using Eq. (319), the time-dependent friction $\eta(t)$ can be expressed in terms of the inverse Fourier cosine transform of the spectral density $J(\omega)$ as

$$\eta(t) = \frac{2}{\pi} \int_{-\infty}^{\infty} \frac{J(\omega)}{\omega} \cos \omega t \, d\omega \quad (321)$$

Now it is possible to obtain the continuum limit for the dynamics by defining $J(\omega)$ as a continuous function instead of defining each amplitude C_j separately [22]. We now take the Laplace transform of $\eta(t)$, that is,

$$\tilde{\eta}(s) = \int_0^{\infty} e^{-st} \eta(t) \, dt \quad (322)$$

so that with Eq. (321)

$$\tilde{\eta}(s) = \frac{2}{\pi} \int_0^{\infty} e^{-st} \int_{-\infty}^{\infty} \frac{J(\omega)}{\omega} \cos \omega t \, d\omega \, dt = \frac{2}{\pi} \int_{-\infty}^{\infty} \frac{s}{\omega (s^2 + \omega^2)} J(\omega) \, d\omega \quad (323)$$

By using Eq. (319), the Laplace transform $\tilde{\eta}(s)$ may be written as

$$\tilde{\eta}(s) = \sum_{j=1}^N \frac{C_j^2}{m_j \omega_j^2} \left(\frac{s}{s^2 + \omega_j^2} \right) \quad (324)$$

We wish to calculate the quantum escape rate and do so as follows. First, the Hamiltonian given in Eq. (318) may be regarded as a quantum Hamiltonian. For a finite discrete set of oscillators one may then evaluate the thermal decay rate using harmonic quantum TST as mentioned in the Introduction. Having obtained the TST expression one may take the continuum limit, so yielding an estimate for the quantum IHD escape rate of particles governed by the generalized Langevin equation.

To implement this, we must according to harmonic TST Eqs. (6) and (18), and the generalized Kramers–Langer–Grote–Hynes expression (58) evaluate the quantum partition functions at the well ($q = 0$) and the barrier ($q = q_{\#}$). The partition functions may be evaluated via a normal mode analysis at the barrier and the well. To derive the rate expression essentially using Eq. (58), we first undertake the normal mode analysis. We assume that the potential may be approximated as

$$V(q) \approx \frac{1}{2} M \omega_0^2 q^2 \quad (325)$$

in the vicinity of the well and as

$$V(q) \approx V^\# - \frac{1}{2}M\omega_\#^2(q - q_\#)^2 \quad (326)$$

at the barrier. Here, ω_0 is the frequency at the well and $\omega_\#$ is the imaginary frequency at the barrier. The harmonic approximations embodied in Eqs. (325) and (326) imply that the Hamiltonian in the vicinity of the well and barrier may be written in *separable form* like in Eq. (6) as that of a sum of $N + 1$ harmonic oscillators. This is achieved [153] by first transforming to mass-weighted coordinates

$$q' = M^{1/2}q, \quad x'_j = m_j^{1/2}x_j \quad (327)$$

and then diagonalizing the $(N + 1) \times (N + 1)$ force constant (Hessian) matrix defined by the second derivatives of the potential at the well and the barrier (cf. Section II.A.4).

The Hamiltonian equation (318) with Eq. (325) becomes

$$H = \frac{p_q^2}{2M} + \frac{M\omega_0^2 q^2}{2} + \sum_{j=1}^N \left[\frac{p_j^2}{2m_j} + \frac{1}{2} \left(m_j^{1/2} \omega_j x_j + \frac{C_j}{m_j^{1/2} \omega_j} q \right)^2 \right] \quad (328)$$

and with Eq. (327) it is now

$$H = \frac{p_q^2}{2M} + \frac{1}{2}\omega_0^2 q'^2 + \sum_{j=1}^N \left[\frac{p_j^2}{2m_j} + \frac{1}{2} \left(x'_j \omega_j + \frac{C_j}{m_j^{1/2} M^{1/2} \omega_j} q' \right)^2 \right] \quad (329)$$

From this equation and Eq. (325) it is clear that the well is located at $q' = x'_j = 0$; $j = 1, \dots, N$.

The second-derivative (Hessian) matrix of the potential (with respect to the mass-weighted coordinates) at the well is denoted by \mathbf{K} and has the following structure

$$\mathbf{K} = \begin{pmatrix} H''_{q',q'} & H''_{q',x'_1} & H''_{q',x'_2} & \cdots & H''_{q',x'_N} \\ H''_{x'_1,q'} & H''_{x'_1,x'_1} & H''_{x'_1,x'_2} & \cdots & H''_{x'_1,x'_N} \\ H''_{x'_2,q'} & H''_{x'_2,x'_1} & H''_{x'_2,x'_2} & \cdots & H''_{x'_2,x'_N} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ H''_{x'_N,q'} & H''_{x'_N,x'_1} & H''_{x'_N,x'_2} & \cdots & H''_{x'_N,x'_N} \end{pmatrix} \quad (330)$$

where the derivatives of H are

$$H''_{q',q'} = \omega_0^2 + \sum_{j=1}^N \frac{C_j^2}{Mm_j\omega_j^2} \quad (331)$$

$$H''_{x'_j,q'} = H''_{q',x'_j} = \frac{C_j}{M^{1/2}m_j^{1/2}}, \quad j = 1, 2, \dots, N \quad (332)$$

and

$$H''_{x'_i,x'_j} = \omega_j^2 \delta_{ij}, \quad i, j = 1, 2, \dots, N \quad (333)$$

Thus, we have the Hessian matrix

$$\mathbf{K} = \begin{pmatrix} \omega_0^2 + \sum_{j=1}^N \frac{C_j^2}{Mm_j\omega_j^2} & \frac{C_1}{(Mm_1)^{1/2}} & \frac{C_2}{(Mm_2)^{1/2}} & \cdots & \frac{C_N}{(Mm_N)^{1/2}} \\ \frac{C_1}{(Mm_1)^{1/2}} & \omega_1^2 & 0 & \cdots & 0 \\ \frac{C_2}{(Mm_2)^{1/2}} & 0 & \omega_2^2 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \frac{C_N}{(Mm_N)^{1/2}} & 0 & 0 & \cdots & \omega_N^2 \end{pmatrix} \quad (334)$$

We have $N + 1$ equations and the $N + 1$ eigenvalues of \mathbf{K} are denoted by λ_i^2 ; $i = 0, 1, \dots, N$. The λ_i are the normal mode frequencies in the well. The matrix \mathbf{K} reads in the diagonal basis

$$\mathbf{K}' = \begin{pmatrix} \lambda_0^2 & 0 & \cdots & 0 \\ 0 & \lambda_1^2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \lambda_N^2 \end{pmatrix} \quad (335)$$

Now in accordance with Eq. (58), consider the determinants of the matrices $\mathbf{K}' + s^2 \mathbf{I}$ and $\mathbf{K} + s^2 \mathbf{I}$ (\mathbf{I} is the $(N + 1) \times (N + 1)$ identity matrix) that are

$$\det[\mathbf{K}' + s^2 \mathbf{I}] = \left(\lambda_0^2 + s^2 \right) \prod_{j=1}^N \left(\lambda_j^2 + s^2 \right) \quad (336)$$

$$\begin{aligned} \det[\mathbf{K} + s^2\mathbf{I}] &= \left(\omega_0^2 + s^2 + \sum_{j=1}^N \frac{C_j^2}{Mm_j\omega_j^2} - \sum_{j=1}^N \frac{C_j^2}{Mm_j(\omega_j^2 + s^2)} \right) \prod_{j=1}^N (\omega_j^2 + s^2) \quad (337) \end{aligned}$$

Using Eq. (324), we then have

$$\begin{aligned} \det[\mathbf{K} + s^2\mathbf{I}] &= \left(\omega_0^2 + s^2 + \frac{s}{M} \sum_{j=1}^N \frac{C_j^2 s}{m_j \omega_j^2 (\omega_j^2 + s^2)} \right) \prod_{j=1}^N (\omega_j^2 + s^2) \\ &= (\omega_0^2 + s^2 + s\tilde{\eta}(s)/M) \prod_{j=1}^N (\omega_j^2 + s^2) \quad (338) \end{aligned}$$

We derive from Eqs. (336) and (338) and since $\det[\mathbf{K}' + s^2\mathbf{I}] = \det[\mathbf{K} + s^2\mathbf{I}]$ (the matrix \mathbf{K}' is the matrix \mathbf{K} in the diagonal basis)

$$\begin{aligned} \det[\mathbf{K} + s^2\mathbf{I}] &= (\lambda_0^2 + s^2) \prod_{j=1}^N (\lambda_j^2 + s^2) \\ &= (\omega_0^2 + s^2 + s\tilde{\eta}(s)/M) \prod_{j=1}^N (\omega_j^2 + s^2) \quad (339) \end{aligned}$$

This is Pollak's equation (13) [18a].

Now the saddle point is located at $q' = q'_\#$ and $x'_j = -[C_j/(m_j M)^{1/2} \omega_j^2] q'_\#$; $j = 1, 2, \dots, N$. The second-derivative matrix at the saddle point, denoted as $\mathbf{K}^\#$ is of the same structure as \mathbf{K} , the only difference is that ω_0^2 is replaced by $-\omega_0^2$. The eigenvalues of $\mathbf{K}^\#$ are denoted by $-\lambda_0^{\#2}, \lambda_j^{\#2}$; $j = 1, 2, \dots, N$. The lowest eigenvalue is as usual (Section II) associated with the unstable mode and is negative [18a]. Using reasoning similar to that used to obtain Eq. (339), we have

$$\begin{aligned} \det[\mathbf{K}^\# + s^2\mathbf{I}] &= (-\lambda_0^{\#2} + s^2) \prod_{j=1}^N (\lambda_j^{\#2} + s^2) \\ &= (-\omega_\#^2 + s^2 + s\tilde{\eta}(s)/M) \prod_{j=1}^N (\omega_j^2 + s^2) \quad (340) \end{aligned}$$

Dividing Eq. (339) by Eq. (340) as required by Eq. (58), we get

$$\frac{\lambda_0^2 + s^2}{-\lambda_0^{\#2} + s^2} \prod_{j=1}^N \frac{\lambda_j^2 + s^2}{\lambda_j^{\#2} + s^2} = \frac{\omega_0^2 + s^2 + s\tilde{\eta}(s)/M}{-\omega_\#^2 + s^2 + s\tilde{\eta}(s)/M}$$

Rearranging we have

$$\prod_{j=1}^N \frac{\lambda_j^2 + s^2}{\lambda_j^{\#2} + s^2} = \left(\frac{-\lambda_0^{\#2} + s^2}{\lambda_0^2 + s^2} \right) \frac{\omega_0^2 + s^2 + s\tilde{\eta}(s)/M}{-\omega_{\#}^2 + s^2 + s\tilde{\eta}(s)/M} \quad (341)$$

This is Pollak's equation (15) [18b].

So far the calculation is entirely classical. Now recalling that in the classical case, the IHD rate is simply the TST rate in the complete phase space of the system we may [cf. Eq. (58)] use a similar argument to calculate the IHD quantum rate from quantum TST.

2. Quantum Transition State Theory

The harmonic transition state theory expression for the rate of decay Γ as mentioned in Section II.A (for detailed proof see [4,154]) is well known:

$$\Gamma = \left(\frac{k_B T}{2\pi\hbar} \right) \frac{Z^{\#}}{Z^0} \quad (342)$$

Here, $Z^{\#}$ and Z^0 are the partition functions at the transition state and at reactants. At the transition state we have N real oscillators with frequencies $\lambda_j^{\#}$; $j = 1, \dots, N$ and one imaginary frequency oscillator with imaginary frequency $\lambda_0^{\#}$. Therefore, the quantum partition function is at the saddle

$$Z^{\#} = \frac{\hbar\lambda_0^{\#}/(2k_B T)}{\sin(\hbar\lambda_0^{\#}/(2k_B T))} e^{-V^{\#}/(k_B T)} \prod_{j=1}^N \frac{1}{2 \sinh(\hbar\lambda_j^{\#}/(2k_B T))} \quad (343)$$

Note the well-known divergence of $Z^{\#}$ at low temperatures [18]. The quantum partition function at the well is

$$Z^0 = \frac{1}{2 \sinh(\hbar\lambda_0/(2k_B T))} e^{-V^0/(k_B T)} \prod_{j=1}^N \frac{1}{2 \sinh(\hbar\lambda_j/(2k_B T))} \quad (344)$$

Therefore, the thermal decay rate, that is, Eq. (342), becomes

$$\Gamma = \frac{\lambda_0^{\#}}{2\pi} \frac{\sinh(\hbar\lambda_0/(2k_B T))}{\sin(\hbar\lambda_0^{\#}/(2k_B T))} e^{-(V^{\#}-V^0)/(k_B T)} \prod_{j=1}^N \frac{\sinh(\hbar\lambda_j/(2k_B T))}{\sinh(\hbar\lambda_j^{\#}/(2k_B T))} \quad (345)$$

We can write this as the *classical* TST rate times a *quantum* correction factor Ξ , namely,

$$\Gamma = \frac{\omega_0}{2\pi} \left(\frac{\lambda_0^\#}{\omega_\#} \right) e^{-(V^\# - V^0)/(k_B T)} \Xi \quad (346)$$

where

$$\Xi = \left(\frac{\omega_\#}{\omega_0} \right) \frac{\sinh(\hbar\lambda_0/(2k_B T))}{\sin(\hbar\lambda_0^\#/(2k_B T))} \prod_{j=1}^N \frac{\sinh(\hbar\lambda_j/(2k_B T))}{\sinh(\hbar\lambda_j^\#/(2k_B T))} \quad (347)$$

Now at very high temperatures we can use the following approximations: $\sinh x \approx x$ and $\sin x \approx x$ for small values of x . Therefore in this limit

$$\Xi \approx \frac{\omega_\#\lambda_0}{\omega_0\lambda_0^\#} \prod_{j=1}^N \frac{\lambda_j}{\lambda_j^\#} \quad (348)$$

Also from Eq. (341) with $s = 0$ we have

$$\prod_{j=1}^N \left(\frac{\lambda_j}{\lambda_j^\#} \right)^2 = \left(\frac{\omega_0\lambda_0^\#}{\omega_\#\lambda_0} \right)^2$$

Rearranging we then have

$$\frac{\omega_\#\lambda_0}{\omega_0\lambda_0^\#} \prod_{j=1}^N \frac{\lambda_j}{\lambda_j^\#} = 1 \quad (349)$$

Thus in the very high-temperature limit, we recover the classical IHD rate in the complete phase space of the particle–bath system, that is, the Kramers–Grote–Hynes rate expression [2] for general memory friction. To evaluate Ξ in the general case, Pollak used the following identities [77]

$$\sinh x = x \prod_{k=1}^{\infty} \left(1 + \frac{x^2}{k^2\pi^2} \right), \quad \sin x = x \prod_{k=1}^{\infty} \left(1 - \frac{x^2}{k^2\pi^2} \right)$$

Using these, we then have

$$\frac{\sinh(\hbar\lambda_j/(2k_B T))}{\sinh(\hbar\lambda_j^\#/(2k_B T))} = \frac{\lambda_j}{\lambda_j^\#} \prod_{k=1}^{\infty} \frac{k^2 v^2 + \lambda_j^2}{k^2 v^2 + \lambda_j^{\#2}}$$

where $\nu = 2\pi k_B T/\hbar$, Eq. (347) may now be written as

$$\begin{aligned}\mathbb{E} &= \frac{\omega_{\#}}{\omega_0} \left(\frac{\lambda_0}{\lambda_0^{\#}} \prod_{k=1}^{\infty} \frac{k^2 \nu^2 + \lambda_0^2}{k^2 \nu^2 - \lambda_0^{\#2}} \right) \prod_{j=1}^N \left(\frac{\lambda_j}{\lambda_j^{\#}} \prod_{k=1}^{\infty} \frac{k^2 \nu^2 + \lambda_j^2}{k^2 \nu^2 + \lambda_j^{\#2}} \right) \\ &= \frac{\omega_{\#} \lambda_0}{\omega_0 \lambda_0^{\#}} \left(\prod_{j=1}^N \frac{\lambda_j}{\lambda_j^{\#}} \right) \left(\prod_{k=1}^{\infty} \frac{k^2 \nu^2 + \lambda_0^2}{k^2 \nu^2 - \lambda_0^{\#2}} \right) \prod_{j=1}^N \left(\prod_{k=1}^{\infty} \frac{k^2 \nu^2 + \lambda_j^2}{k^2 \nu^2 + \lambda_j^{\#2}} \right)\end{aligned}\quad (350)$$

Insertion of Eq. (349) in Eq. (350) yields

$$\mathbb{E} = \prod_{k=1}^{\infty} \left[\frac{k^2 \nu^2 + \lambda_0^2}{k^2 \nu^2 - \lambda_0^{\#2}} \prod_{j=1}^N \left(\frac{k^2 \nu^2 + \lambda_j^2}{k^2 \nu^2 + \lambda_j^{\#2}} \right) \right]\quad (351)$$

Using Eq. (341) with $s = kv$, where the kv are called the Matsubara (bosonic) frequencies, we have

$$\prod_{j=1}^N \frac{k^2 \nu^2 + \lambda_j^2}{k^2 \nu^2 + \lambda_j^{\#2}} = \frac{\omega_0^2 + k^2 \nu^2 + (kv/M)\tilde{\eta}(kv)}{-\omega_{\#}^2 + k^2 \nu^2 + (kv/M)\tilde{\eta}(kv)} \left(\frac{-\lambda_0^{\#2} + k^2 \nu^2}{\lambda_0^2 + k^2 \nu^2} \right)\quad (352)$$

Substituting the right-hand side of Eq. (352) in Eq. (351), we finally have the quantum correction factor

$$\mathbb{E} = \prod_{k=1}^{\infty} \frac{\omega_0^2 + k^2 \nu^2 + (kv/M)\tilde{\eta}(kv)}{-\omega_{\#}^2 + k^2 \nu^2 + (kv/M)\tilde{\eta}(kv)}\quad (353)$$

3. Transition Probability (Semiclassical Green Function)

To consider the quantum problem in the underdamped regime, we essentially follow the route described in the classical case. Our task, mirroring the classical one, is the derivation of the statistical density matrix associated with the evolution operator $\hat{\Phi}(t)$ in the well in the presence of quantum noise, which is the quantum analog of the Green function (94) describing the alteration in energy in one cycle of the periodic motion in the well on trajectories infinitesimally close to the separatrix trajectory. In like manner the operator $\hat{\Phi}(t)$ describes the evolution of the (noisy) state vector, in the interaction representation, in one cycle of the periodic motion in the well on trajectories infinitesimally close to the separatrix trajectory. The density matrix that is determined by the matrix elements of $\hat{\Phi}(t)$ will then be rendered in semiclassical fashion in terms of Fourier transforms as the inverse Fourier transform of a characteristic function using the properties of the noise. We proceed in the systematic way proposed by Larkin and Ovchinnikov [11]. Thus,

we suppose that the Hamiltonian of a quantum particle, interacting with a thermal bath, may be represented as

$$\hat{H}(t) = \hat{H}_0(x) + \hat{x}\hat{\eta} \quad (354)$$

where $\hat{H}_0(x) = \hat{p}^2/2m + V(x)$ is the unperturbed Hamiltonian of the particle with coordinate x , executing classically a librational trajectory with energy equal to the barrier energy in the well potential that we denote by $V(x)$, the term $\hat{x}\hat{\eta}$ describes an interaction with the heat bath that is supposed linear in the particle coordinate x . It is assumed that the noise operator $\hat{\eta}$ is centered Gaussian with spectral density given by (we are dealing with Johnson–Nyquist noise so that we have a Boson bath)

$$D(\Omega) = \int_{-\infty}^{\infty} \langle \hat{\eta}(t)\hat{\eta}(t + \tau) \rangle_T e^{i\Omega\tau} d\tau = m\beta\hbar\Omega[\coth(\hbar\Omega/(2k_B T)) - 1] \quad (355)$$

and $\langle \hat{\eta}(t) \rangle_T = 0$, where the subscript T denotes averaging over the heat bath states. In the classical limit $\hbar \rightarrow 0$, this becomes the usual white noise spectral density $D = 2m\beta k_B T$.

The first step in the calculation of the density matrix is to determine the solution $\psi(t)$ of the time-dependent Schrödinger equation pertaining to the noise-perturbed librational motion in the well, namely

$$i\hbar \frac{\partial \psi}{\partial t} = (\hat{H}_0(x) + \hat{x}\hat{\eta}) \psi \quad (356)$$

using time-dependent perturbation theory. Consider the Hamiltonian \hat{H} given by

$$\hat{H} = \hat{H}_0 + \xi \hat{x}' \hat{\eta}', \quad \hat{x}' \hat{\eta}' = \hat{x}\hat{\eta}/\xi \quad (357)$$

Here, \hat{H} is the sum of the unperturbed Hamiltonian \hat{H}_0 and the (weak) noise perturbation $\xi \hat{x}' \hat{\eta}'$. The effect of $\xi \hat{x}' \hat{\eta}'$ is to perturb the time evolution of \hat{H}_0 . Let $\psi(t)$ denote the solution of the Schrödinger equation (356)

$$i\hbar \frac{\partial \psi}{\partial t} = (\hat{H}_0(x) + \xi \hat{x}' \hat{\eta}') \psi \quad (358)$$

with $\xi \ll 1$. We assume that we can expand the perturbed wave function $\psi(t)$ as a power series in ξ

$$\psi(t) = \psi_0(t) + \xi \psi_1(t) + \xi^2 \psi_2(t) + \dots \quad (359)$$

Thus, we have the system

$$i\hbar \frac{\partial \psi_0}{\partial t} = \hat{H}_0 \psi_0 \quad (360)$$

$$i\hbar \frac{\partial \psi_i}{\partial t} = \hat{H}_0 \psi_i + \hat{x}' \hat{\eta}' \psi_{i-1}, \quad i = 1, 2, \dots \quad (361)$$

with successive approximation solution

$$\psi_0(t) = e^{-(i/\hbar)\hat{H}_0 t} \psi_0(0) \quad (362)$$

$$\psi_1(t) = e^{-(i/\hbar)\hat{H}_0 t} \psi_1(0) - \frac{i}{\hbar} e^{-(i/\hbar)\hat{H}_0 t} \int_0^t \hat{x}'(t_1) \hat{\eta}'(t_1) dt_1 \psi_0(0) \quad (363)$$

$$\begin{aligned} \psi_2(t) = & e^{-(i/\hbar)\hat{H}_0 t} \psi_2(0) - \frac{i}{\hbar} e^{-(i/\hbar)\hat{H}_0 t} \int_0^t \hat{x}'(t_1) \hat{\eta}'(t_1) dt_1 \psi_1(0) \\ & - \frac{1}{\hbar^2} e^{-(i/\hbar)\hat{H}_0 t} \int_0^t \hat{x}'(t_1) \hat{\eta}'(t_1) \int_0^{t_1} \hat{x}'(t_2) \hat{\eta}'(t_2) dt_2 dt_1 \psi_0(0) \end{aligned} \quad (364)$$

where $\hat{x}'(t) = e^{iH_0 t/\hbar} \hat{x}' e^{-iH_0 t/\hbar}$ and $\hat{\eta}'(t) = e^{iH_0 t/\hbar} \hat{\eta}' e^{-iH_0 t/\hbar}$ are operators in the interaction representation.

Thus, the general solution of Eq. (358) is the series

$$\begin{aligned} \psi(t) = & e^{-(i/\hbar)\hat{H}_0 t} \left[\psi_0(0) + \xi \psi_1(0) + \xi^2 \psi_2(0) + \dots \right] \\ & - \xi \frac{i}{\hbar} e^{-(i/\hbar)\hat{H}_0 t} \int_0^t \hat{x}'(t_1) \hat{\eta}'(t_1) dt_1 [\psi_0(0) + \xi \psi_1(0) + \dots] \\ & - \xi^2 \frac{1}{\hbar^2} e^{-(i/\hbar)\hat{H}_0 t} \int_0^t \hat{x}'(t_1) \hat{\eta}'(t_1) \int_0^{t_1} \hat{x}'(t_2) \hat{\eta}'(t_2) dt_2 dt_1 [\psi_0(0) + \dots] \end{aligned} \quad (365)$$

or, equivalently,

$$\begin{aligned} \psi(t) = & e^{-(i/\hbar)\hat{H}_0 t} \left(1 - \frac{i}{\hbar} \int_0^t \hat{x}(t_1) \hat{\eta}(t_1) dt_1 \right. \\ & \left. - \frac{1}{\hbar^2} \int_0^t \hat{x}(t_1) \hat{\eta}(t_1) \int_0^{t_1} \hat{x}(t_2) \hat{\eta}(t_2) dt_2 dt_1 + \dots \right) \psi(0) \\ = & e^{-(i/\hbar)\hat{H}_0 t} \left\{ \hat{T} e^{-\frac{i}{\hbar} \int_0^t \hat{x}(t_1) \hat{\eta}(t_1) dt_1} \right\} \psi(0) \end{aligned} \quad (366)$$

Here, \hat{T} is the time ordering operator and $\hat{T} e^{-(i/\hbar)\int_0^t \hat{x}(t_1)\hat{\eta}(t_1)dt_1}$ is defined as

$$\hat{T} e^{-(i/\hbar)\int_0^t \hat{x}(t_1)\hat{\eta}(t_1)dt_1} = \left(1 - \frac{i}{\hbar} \int_0^t \hat{x}(t_1)\hat{\eta}(t_1) dt_1 - \frac{1}{\hbar^2} \int_0^t \hat{x}(t_1)\hat{\eta}(t_1) \int_0^{t_1} \hat{x}(t_2)\hat{\eta}(t_2) dt_2 dt_1 + \dots \right) \quad (367)$$

In Dirac notation, we have in terms of the evolution of the state vector $|\psi\rangle$

$$|\psi(t)\rangle = e^{-(i/\hbar)\hat{H}_0 t} \hat{\Phi}(t) |\psi(0)\rangle \quad (368)$$

If $\psi_j(x, t)$ denotes the wavefunction of the *unperturbed* state j , then the matrix elements, $A_{jf} = \langle f | \hat{\Phi}(t) | j \rangle$, of the evolution operator $\hat{\Phi}(t)$ in the basis $\{\psi_j(x, t)\}$ of the unperturbed states represent the amplitudes of noise-induced transitions from energy state E_j to energy state E_f , namely,

$$\begin{aligned} A_{jf} &= \langle f | \left(1 - \frac{i}{\hbar} \int_0^t \hat{x}(t_1)\hat{\eta}(t_1) dt_1 - \frac{1}{\hbar^2} \int_0^t \hat{x}(t_1)\hat{\eta}(t_1) \int_0^{t_1} \hat{x}(t_2)\hat{\eta}(t_2) dt_2 dt_1 + \dots \right) | j \rangle \\ &= \left(\delta_{jf} - \frac{i}{\hbar} \int_0^t \langle f | \hat{x}(t_1) | j \rangle \eta(t_1) dt_1 - \frac{1}{\hbar^2} \sum_n \int_0^t \langle f | \hat{x}(t_1) | n \rangle \hat{\eta}(t_1) \right. \\ &\quad \left. \times \int_0^{t_1} \langle n | \hat{x}(t_2) | j \rangle \hat{\eta}(t_2) dt_2 dt_1 + \dots \right) \end{aligned} \quad (369)$$

where we have used $\sum_n |n\rangle \langle n| = \hat{I}$, the identity operator to write

$$\langle f | \hat{x}(t_1)\hat{x}(t_2) | j \rangle = \sum_n \langle f | \hat{x}(t_1) | n \rangle \langle n | \hat{x}(t_2) | j \rangle$$

In order to simplify Eq. (369) via semiclassical approximation we first recall that since the (upper) energy levels in the well near a classical turning point such as the barrier energy of the potential are quasicontinuous, the matrix elements of the position operator $\hat{x}(t)$ are given by the semiclassical formula [8,11,19] essentially based on the JWKB approximation (for an elementary justification see Appendix E)

$$\langle f | \hat{x}(t) | j \rangle = \frac{\omega}{2\pi} \oint x_j(\tau) e^{-(i/\hbar)(E_f - E_j)(\tau - t)} d\tau \quad (370)$$

Here, the appropriate domain of integration is over a cycle of the classical librational motion of the particle with energy equal to the barrier energy and angular frequency ω . Therefore, Eq. (370) simply represents the Fourier coefficients of the Fourier series representation of the (periodic) classical trajectories in terms of the matrix elements of the operator $\hat{x}(t)$ that we shall make more use of below. In addition, the semiclassical representation of the matrix elements of $\hat{x}(t)$ suggests because the motion of the particle in the well is periodic that we can also regard the amplitudes $A_{jf} = \langle f | \hat{\Phi}(t) | j \rangle$ of the noise-induced transitions (or matrix elements of $\hat{\Phi}(t)$) that are given by Eq. (369) as simply the Fourier coefficients in the Fourier series representation of yet another periodic function $A(u)$, namely,

$$A(u) = \sum_f A_{jf} e^{(i/\hbar)(E_f - E_j)u} \quad (371)$$

$$A_{jf} = \frac{\omega}{2\pi} \oint A(u) e^{-(i/\hbar)(E_f - E_j)u} du \quad (372)$$

Furthermore, the classical librational motion with energy equal to the barrier energy represents the slowest librational motion in the well (period–amplitude dependence of an anharmonic oscillator) so that for many purposes [8] a particle executing this slow cycle may be regarded (see Fig. 3) as starting from the point $x = 0$ at $t = -\infty$ and returning to that point as $t \rightarrow \infty$. The importance of this observation is that Fourier series like Eq. (371) in the present context go smoothly over into Fourier integrals.

Now our immediate objective is to derive in semiclassical fashion a closed form expression for $A(u)$ analogous to the closed form Eq. (367) that will then be used to calculate the Green function (statistical density matrix) using the properties of the Gaussian noise operator $\hat{\eta}(t)$. First we substitute expansion (369) into Eq. (371). We then have the series

$$A(u) = \sum_f e^{(i/\hbar)(E_f - E_j)u} \left\{ \delta_{jf} - \frac{i}{\hbar} \int_0^t \langle f | \hat{x}(t_1) | j \rangle \hat{\eta}(t_1) dt_1 \right. \\ \left. - \frac{1}{\hbar^2} \sum_n \int_0^t \langle f | \hat{x}(t_1) | n \rangle \hat{\eta}(t_1) \int_0^{t_1} \langle n | \hat{x}(t_2) | j \rangle \hat{\eta}(t_2) dt_2 dt_1 + \dots \right\} \quad (373)$$

Our objective will now be accomplished if we can find (in the semiclassical sense) the sum of this series. This is done as follows using the semiclassical representation of the matrix elements $\langle f | \hat{x}(t) | j \rangle$ of the position operator $\hat{x}(t)$ as the Fourier

transform of the classical librational trajectory equation (370). First we rewrite Eq. (373) as

$$\begin{aligned}
A(u) = & \sum_f e^{(i/\hbar)(E_f - E_j)u} \left\{ \delta_{jf} - \frac{i}{\hbar} \frac{\omega}{2\pi} \int_0^t \hat{\eta}(t_1) \oint x_j(\tau) e^{-(i/\hbar)(E_f - E_j)(\tau - t_1)} d\tau dt_1 \right. \\
& - \frac{1}{\hbar^2} \left(\frac{\omega}{2\pi} \right)^2 \sum_n \int_0^t \oint x_n(\tau_1) e^{-(i/\hbar)(E_f - E_n)(\tau_1 - t_1)} d\tau_1 \hat{\eta}(t_1) \\
& \left. \times \int_0^{t_1} \oint x_j(\tau_2) e^{-(i/\hbar)(E_n - E_j)(\tau_2 - t_2)} d\tau_2 \hat{\eta}(t_2) dt_2 dt_1 + \dots \right\} \quad (374)
\end{aligned}$$

However, due to the elementary shifting properties

$$e^{(i/\hbar)(E_f - E_i)u} \delta_{if} = \delta_{if} \quad (375)$$

$$e^{(i/\hbar)(E_f - E_i)u} e^{-(i/\hbar)(E_f - E_i)(\tau - t_1)} = e^{-(i/\hbar)(E_f - E_i)(\tau - t_1 - u)} \quad (376)$$

$$\begin{aligned}
& e^{(i/\hbar)(E_f - E_i)u} e^{-(i/\hbar)(E_f - E_n)(\tau_1 - t_1)} e^{-(i/\hbar)(E_n - E_i)(\tau_2 - t_2)} \\
& = e^{-(i/\hbar)(E_f - E_n)(\tau_1 - t_1 - u)} e^{-(i/\hbar)(E_n - E_i)(\tau_2 - t_2 - u)} \quad (377)
\end{aligned}$$

Equation (374) can also be rewritten as

$$\begin{aligned}
A(u) = & \sum_f \left\{ \delta_{jf} - \frac{i}{\hbar} \frac{\omega}{2\pi} \int_0^t \hat{\eta}(t_1) \oint x_j(\tau) e^{-(i/\hbar)(E_f - E_j)(\tau - t_1 - u)} d\tau dt_1 \right. \\
& - \frac{1}{\hbar^2} \left(\frac{\omega}{2\pi} \right)^2 \sum_n \int_0^t \hat{\eta}(t_1) \oint x_n(\tau_1) e^{-(i/\hbar)(E_f - E_n)(\tau_1 - t_1 - u)} d\tau_1 \\
& \left. \times \int_0^{t_1} \hat{\eta}(t_2) \oint x_j(\tau_2) e^{-(i/\hbar)(E_n - E_j)(\tau_2 - t_2 - u)} d\tau_2 dt_2 dt_1 + \dots \right\} \quad (378)
\end{aligned}$$

Next in order to sum this series, we note that the semiclassical matrix elements decrease rapidly with the energy difference $E_f - E_j$. Moreover, they are smooth functions of the energy E_j of the unperturbed state [11] meaning that $E_n \sim E_j$

so that we may substitute x_j for x_n in the third term on the right-hand side of Eq. (378). Hence that equation can now be rewritten as the time ordered exponential

$$\begin{aligned}
A(u) &= \sum_f \left(\delta_{jf} - \frac{i}{\hbar} \int_0^t \langle f | \hat{x}(t_1 + u) | j \rangle \hat{\eta}(t_1) dt_1 \right. \\
&\quad \left. - \frac{1}{\hbar^2} \sum_n \int_0^t \langle f | \hat{x}(t_1 + u) | n \rangle \hat{\eta}(t_1) \int_0^{t_1} \langle n | \hat{x}(t_2 + u) | j \rangle \hat{\eta}(t_2) dt_2 dt_1 + \dots \right) \\
&= \sum_f \left(\delta_{jf} - \frac{i}{\hbar} \int_0^t x_j(t_1 + u) \langle f | j \rangle \hat{\eta}(t_1) dt_1 \right. \\
&\quad \left. - \frac{1}{\hbar^2} \sum_n \int_0^t x_n(t_1 + u) \langle f | n \rangle \hat{\eta}(t_1) \int_0^{t_1} x_j(t_2 + u) \langle n | j \rangle \hat{\eta}(t_2) dt_2 dt_1 + \dots \right) \\
&= \left(1 - \frac{i}{\hbar} \int_0^t x_j(t_1 + u) \hat{\eta}(t_1) dt_1 - \frac{1}{\hbar^2} \int_0^t x_j(t_1 + u) \hat{\eta}(t_1) \right. \\
&\quad \left. \times \int_0^{t_1} x_j(t_2 + u) \hat{\eta}(t_2) dt_2 dt_1 + \dots \right) \tag{379}
\end{aligned}$$

that is, the sum becomes

$$A(u) = \hat{T} e^{-(i/\hbar) \int_0^t x_j(u+t_1) \eta(t_1) dt_1} \tag{380}$$

which is the desired closed integral form expression for the Fourier expansion of the periodic function $A(u)$. Now the Fourier coefficients A_{jf} simply represent the matrix elements of the evolution operator $\hat{\Phi}$ for the state vector. Hence, the probability of a transition from state j to state f during a time interval t described by $\hat{\Phi}$ and averaged over the bath states denoted by $\langle \rangle_T$ that is the statistical density matrix, can be represented in terms of probability amplitudes as

$$W_{jf} = \langle |A_{jf}|^2 \rangle_T = \langle A_{jf} A_{jf}^* \rangle_T \tag{381}$$

where A_{jf} is given by Eq. (372). However using the Fourier coefficients, Eq. (372), we may also rewrite the density matrix Eq. (381) in terms of the Fourier expansion $A(u)$ as follows

$$\begin{aligned} W_{jf} &= \left\langle \left(\frac{\omega}{2\pi} \right)^2 \oint A(u_1) e^{-(i/\hbar)(E_f - E_j)u_1} du_1 \oint A^*(u_2) e^{(i/\hbar)(E_f - E_j)u_2} du_2 \right\rangle_T \\ &= \left\langle \left(\frac{\omega}{2\pi} \right)^2 \oint \oint e^{-(i/\hbar)(E_f - E_j)(u_1 - u_2)} A(u_1) A^*(u_2) du_2 du_1 \right\rangle_T \end{aligned} \quad (382)$$

Hence, we have the key equation for the density matrix (Green function)

$$W_{jf} = \left(\frac{\omega}{2\pi} \right)^2 \oint du_1 \oint du_2 e^{-(i/\hbar)(E_f - E_j)(u_1 - u_2)} \langle A(u_1) A^*(u_2) \rangle_T \quad (383)$$

which formally represents the semiclassical transition probability associated with the evolution operator $\hat{\Phi}$. Next to find the correlation function $\langle A(u_1) A^*(u_2) \rangle_T$ explicitly, we use the sum, Eq. (380), to substitute for $A(u)$ in Eq. (383) so that formally

$$\begin{aligned} \langle A(u_1) A^*(u_2) \rangle_T &= \left\langle \hat{T} \exp \left[-\frac{i}{\hbar} \left(\int_0^t x_j(u_1 + t') \hat{\eta}(t') dt' \right) \right] \right. \\ &\quad \left. \times \hat{T} \exp \left[\frac{i}{\hbar} \left(\int_0^t x_j(u_2 + t'') \hat{\eta}(t'') dt'' \right) \right] \right\rangle_T \end{aligned} \quad (384)$$

Now we have assumed that the Johnson–Nyquist noise is zero-mean Gaussian. Hence to simplify Eq. (384), we can utilize (remembering that linear transformations of Gaussian random variables are themselves Gaussian) the characteristic function of the centered Gaussian random variables z_1 and z_2 , namely,

$$\langle e^{i(z_2 - z_1)} \rangle_T = e^{(1/2)(\langle z_1^2 \rangle_T + \langle z_2^2 \rangle_T - \langle z_1 z_2 \rangle_T - \langle z_2 z_1 \rangle_T)} \quad (385)$$

where

$$z_{1,2} = \frac{1}{\hbar} \left(\int_0^t x_j(u_{1,2} + t') \hat{\eta}(t') dt' \right)$$

We have

$$\begin{aligned} & \left\langle \left[\frac{1}{\hbar} \left(\int_0^t x_j(u_1 + t') \hat{\eta}(t') dt' \right) \right]^2 \right\rangle_T \\ &= \frac{1}{\hbar^2} \left(\int_0^t \int_0^t x_j(u_1 + t_1) x_j(u_1 + t_2) \langle \hat{T} \hat{\eta}(t_1) \hat{\eta}(t_2) \rangle_T dt_1 dt_2 \right) \end{aligned} \quad (386)$$

where the time-ordering operator \hat{T} ensures that integration with respect to t_1 is carried out first. In like manner

$$\begin{aligned} & \left\langle \left[\frac{1}{\hbar} \left(\int_0^t x_j(u_2 + t'') \hat{\eta}(t'') dt'' \right) \right]^2 \right\rangle_T \\ &= \frac{1}{\hbar^2} \left(\int_0^t \int_0^t x_j(u_2 + t_1) x_j(u_2 + t_2) \langle \hat{T} \hat{\eta}(t_1) \hat{\eta}(t_2) \rangle_T dt_1 dt_2 \right) \quad (387) \\ &= \frac{1}{\hbar^2} \left(\int_0^t \int_0^t x_j(u_2 + t_1) x_j(u_2 + t_2) \langle \hat{T}^{-1} \hat{\eta}(t_2) \hat{\eta}(t_1) \rangle_T dt_1 dt_2 \right) \end{aligned}$$

where \hat{T}^{-1} ensures that the integration with respect to t_2 is now carried out first. Likewise

$$\begin{aligned} & \left\langle \frac{1}{\hbar^2} \left(\int_0^t x_j(u_1 + t') \hat{\eta}(t') dt' \right) \left(\int_0^t x_j(u_2 + t'') \hat{\eta}(t'') dt'' \right) \right\rangle_T \\ &= \frac{1}{\hbar^2} \left(\int_0^t \int_0^t x_j(u_1 + t_1) x_j(u_2 + t_2) \langle \hat{\eta}(t_1) \hat{\eta}(t_2) \rangle_T dt_1 dt_2 \right), \end{aligned} \quad (388)$$

$$\begin{aligned} & \left\langle \frac{1}{\hbar^2} \left(\int_0^t x_j(u_2 + t'') \hat{\eta}(t'') dt'' \right) \left(\int_0^t x_j(u_1 + t') \hat{\eta}(t') dt' \right) \right\rangle_T \\ &= \frac{1}{\hbar^2} \left(\int_0^t \int_0^t x_j(u_2 + t_2) x_j(u_1 + t_1) \langle \hat{\eta}(t_2) \hat{\eta}(t_1) \rangle_T dt_1 dt_2 \right) \end{aligned} \quad (389)$$

Hence, Eq. (383) now reduces to the explicit form [note that $W_{jf} = W_{jf}(E_f - E_j)$]

$$\begin{aligned}
W_{jf} &= \left(\frac{\omega}{2\pi}\right)^2 \oint \oint e^{-(i/\hbar)(u_1 - u_2)(E_f - E_j)} \\
&\times \exp \left\{ -\frac{1}{2\hbar^2} \left\{ \int_0^t \int_0^t [x_j(u_1 + t_1)x_j(u_1 + t_2)h_{11}(t_1, t_2) \right. \right. \\
&+ x_j(u_2 + t_1)x_j(u_2 + t_2)h_{22}(t_1, t_2) - x_j(u_1 + t_1)x_j(u_2 + t_2)h_{12}(t_1, t_2) \\
&\left. \left. - x_j(u_2 + t_1)x_j(u_1 + t_2)h_{21}(t_1, t_2)] dt_1 dt_2 \right\} du_2 du_1 \right\} \quad (390)
\end{aligned}$$

where the noise correlation functions $h_{rs}(t_1, t_2)$ are given by

$$h_{11}(t_1, t_2) = \langle \hat{T} \hat{\eta}(t_1) \hat{\eta}(t_2) \rangle_T, \quad h_{22}(t_1, t_2) = \langle \hat{T}^{-1} \hat{\eta}(t_2) \hat{\eta}(t_1) \rangle_T \quad (391)$$

$$h_{12}(t_1, t_2) = \langle \hat{\eta}(t_1) \hat{\eta}(t_2) \rangle_T, \quad h_{21}(t_1, t_2) = \langle \hat{\eta}(t_2) \hat{\eta}(t_1) \rangle_T \quad (392)$$

The expression for the statistical density matrix (390) may now be reduced to the inverse Fourier transform of a characteristic function essentially because the correlation functions h depend only on the time difference $t_1 - t_2$ and vanish outside a narrow region $|t_1 - t_2| \sim \hbar/(k_B T)$, that is, they resemble delta functions. These properties will be used to simplify Eq. (390) but first we must consider the matrix elements of the position operator products in the form in which they occur in Eq. (390). The matrix elements of $\hat{x}(t)$ will be given by the semiclassical expression (370) so that as consistent with the Fourier series expansion embodied in Eqs. (371) and (372) [see in particular the note immediately following Eq. (372)] we may write the products of the trajectories occurring in Eq. (390) as the Fourier series

$$\begin{aligned}
x_j(u_1 + t_1) x_j(u_1 + t_2) &= \sum_{fm} \langle f | \hat{x} | j \rangle \langle m | \hat{x} | j \rangle^* e^{(i/\hbar)(E_f - E_j)(u_1 + t_1)} \\
&\times e^{-(i/\hbar)(E_m - E_j)(u_1 + t_2)} \\
&= \sum_{fm} \langle f | \hat{x} | j \rangle \langle m | \hat{x} | j \rangle^* e^{(i/\hbar)(E_f - E_j)(t_1 - t_2)} \\
&\times e^{(i/\hbar)(E_f - E_m)(u_1 + t_2)} \quad (393)
\end{aligned}$$

$$\begin{aligned}
&x_j(u_2 + t_1) x_j(u_2 + t_2) \\
&= \sum_{fm} \langle f | \hat{x} | j \rangle \langle m | \hat{x} | j \rangle^* e^{(i/\hbar)(E_f - E_j)(t_1 - t_2)} e^{(i/\hbar)(E_f - E_m)(u_2 + t_2)} \quad (394)
\end{aligned}$$

$$\begin{aligned}
x_j(u_1 + t_1) x_j(u_2 + t_2) &= \sum_{fm} \langle f | \hat{x} | j \rangle \langle m | \hat{x} | j \rangle^* e^{(i/\hbar)(E_f - E_j)(u_1 + t_1)} \\
&\quad \times e^{-(i/\hbar)(E_m - E_j)(u_2 + t_2)} \\
&= \sum_{fm} \langle f | \hat{x} | j \rangle \langle m | \hat{x} | j \rangle^* \\
&\quad \times e^{(i/\hbar)(E_f - E_j)(u_1 - u_2 + t_1 - t_2)} e^{(i/\hbar)(E_f - E_m)(u_2 + t_2)}
\end{aligned} \tag{395}$$

and

$$\begin{aligned}
&x_j(u_2 + t_1) x_j(u_1 + t_2) \\
&= \sum_{fm} \langle f | \hat{x} | j \rangle^* \langle m | \hat{x} | j \rangle e^{(i/\hbar)(E_f - E_j)(u_1 - u_2 + t_2 - t_1)} e^{(i/\hbar)(E_f - E_m)(u_2 + t_1)}
\end{aligned} \tag{396}$$

Since we have reverted from representations as trajectories to quantum operator representations here we must use the complex conjugate [cf. Eq. (384)]. Next, we substitute Eqs. (393)–(396) in Eq. (390) noting that by orthogonality

$$\oint e^{(i/\hbar)(E_f - E_m)t} dt = \frac{2\pi}{\omega} \delta_{fm}$$

This fact coupled with the anticipated (cf. Eq. (355) and its classical limit) rapid decrease of the noise correlation functions h enables us to extend the integrations over the time difference $t_1 - t_2$ in the exponent of formula (390) to infinite limits so that the exponent in formula (390) is now only a function of the difference $u = u_2 - u_1$. Because [11]

$$h_{11}(t_1 - t_2) + h_{22}(t_1 - t_2) = h_{12}(t_1 - t_2) + h_{21}(t_1 - t_2) \tag{397}$$

Equation (390) for the Green function can then be rewritten as

$$\begin{aligned}
W_{jf} &= \frac{\omega}{2\pi} \oint e^{(i/\hbar)(E_f - E_j)u} \exp \left\{ \frac{2\pi}{\omega} \sum_f |\langle f | \hat{x} | j \rangle|^2 \left[\int_{-\infty}^{\infty} e^{(i/\hbar)(E_f - E_j)(-u + t_1 - t_2)} \right. \right. \\
&\quad \times \frac{h_{21}(t_1 - t_2) + h_{12}(t_1 - t_2)}{2\hbar^2} d(t_1 - t_2) \\
&\quad \left. \left. - \int_{-\infty}^{\infty} e^{(i/\hbar)(E_f - E_j)(t_1 - t_2)} \frac{h_{11}(t_1 - t_2) + h_{22}(t_1 - t_2)}{2\hbar^2} d(t_1 - t_2) \right] \right\} du
\end{aligned} \tag{398}$$

We have again exploited the rapid decrease of h to extend the limits to infinity in the integration with respect to $t_1 - t_2$. By introducing the (time–frequency domain)

Fourier transform of the noise correlation functions $h_{k,l}(t)$

$$\tilde{h}_{k,l}(E_j - E_f) = \int_{-\infty}^{\infty} e^{(i/\hbar)(E_f - E_j)t} h_{k,l}(t) dt \quad (399)$$

we can write

$$\begin{aligned} \int_{-\infty}^{\infty} e^{(i/\hbar)(E_f - E_j)t} \frac{h_{21}(t) + h_{12}(t)}{2\hbar} dt &= \frac{\tilde{h}_{21}(E_f - E_j) + \tilde{h}_{12}(E_j - E_f)}{2\hbar} \\ &= D(E_f - E_j) \end{aligned} \quad (400)$$

with $D(E_f - E_j)$ given by Eq. (355). Using Eq. (400) in Eq. (398), we finally have exactly analogous to Eqs. (92)–(94); the Green function rendered as the inverse Fourier transform of a characteristic function, namely,

$$W_{jf} = \frac{\omega}{2\pi} \oint e^{(i/\hbar)(E_f - E_j)u} \exp\{\wp(u) - \wp(0)\} du = g(E_f - E_j) \quad (401)$$

where the argument $\wp(u)$ is defined by

$$\wp(u) = \sum_f w_{jf} e^{-(i/\hbar)(E_f - E_j)u} = \frac{2\pi}{\hbar\omega} \sum_f |\langle f | \hat{x} | j \rangle|^2 e^{-(i/\hbar)(E_f - E_j)u} D(E_f - E_j) \quad (402)$$

which by definition is simply the Fourier transform of w_{jf} , where

$$w_{jf} = \frac{2\pi}{\hbar\omega} |\langle f | \hat{x} | j \rangle|^2 D(E_f - E_j) \quad (403)$$

represents the quantum probability per cycle (period) of transitions from state j to state f associated with the position operator \hat{x} in the presence of the noise in accordance with first-order perturbation theory (Fermi's Golden Rule) [23]. Note that the Golden Rule probability w_{jf} effectively represents the output spectral density if the Johnson–Nyquist noise is regarded as being passed through a filter with transfer function given by the Fourier transform over the classical trajectories, that is, the matrix elements of the position operator. This concludes our appraisal of the calculation of Larkin and Ovchinnikov [11].

Now in order to compare with Mel'nikov's [8] calculation, we first prove that Eq. (401) yields the first-order perturbation contribution to $g(E_f - E_j)$, we have on expansion of that equation

$$\begin{aligned}
g_1(E_f - E_j) &= \frac{\omega}{2\pi} \oint e^{(i/\hbar)(E_f - E_j)u} [1 + \wp(u) - \wp(0)] du \\
&= \frac{\omega}{2\pi} \oint e^{(i/\hbar)(E_f - E_j)u} \\
&\quad \left(1 + \sum_{f'} w_{jf'} e^{-(i/\hbar)(E_{f'} - E_j)u} - \sum_{f'} w_{jf'} \right) du \\
&= \delta_{fj} + w_{jf} - \delta_{fj} \sum_{f'} w_{jf'} \tag{404}
\end{aligned}$$

Equation (404) should now be compared with Eq. (3.6) of Ref. [8]. Using Mel'nikov's notation in Eq. (403), we make the replacements $E_f \rightarrow \varepsilon$, $E_j \rightarrow \varepsilon'$, $w_{jf} \rightarrow w(\varepsilon - \varepsilon')$ and substitute the Johnson–Nyquist spectral density $D(\varepsilon - \varepsilon')$ rendered by Eq. (355). Then we can rewrite the Golden Rule quantum probability as

$$w(\varepsilon - \varepsilon') = \frac{2\pi}{\hbar} |\langle \varepsilon | \hat{x} | \varepsilon' \rangle|^2 m \gamma(\varepsilon - \varepsilon') [\coth [(\varepsilon - \varepsilon')/(2k_B T)] - 1] \tag{405}$$

The expression for semiclassical Green function $g(\varepsilon - \varepsilon')$ associated with the change in energy in one cycle then becomes [8,9]

$$g(\varepsilon - \varepsilon') = e^{-\int_{-\infty}^{\infty} w(\varepsilon) d\varepsilon} \left\{ w(\varepsilon - \varepsilon') + \frac{1}{2} \int_{-\infty}^{\infty} w(\varepsilon - \varepsilon'') w(\varepsilon'' - \varepsilon') d\varepsilon'' + \dots \right\} \tag{406}$$

which is Mel'nikov's equation (3.9). Now following Mel'nikov [8] we define the Fourier transform via

$$f(\lambda) = \int_{-\infty}^{\infty} f(\varepsilon) e^{i\lambda\varepsilon/(k_B T)} d\varepsilon \tag{407}$$

Thus as shown in Ref. [8], the Fourier transform of the Green function $g(E_f - E_j)$ is

$$g(\lambda) = \exp\{w(\lambda) - w(0)\} \tag{408}$$

where $w(\lambda)$ is the Fourier transform of $w(\varepsilon)$ rendered by Eq. (405) that is the quantum analog of the classical characteristic function derived earlier, Eqs. (92)

and (93) and reduces to these equations at high temperatures as shown by Larkin and Ovchinnikov.

4. Integral Equation and its Solution

In order to write down an integral equation similar to Eq. (101) for the population of escaping particles we recall that in a quantum situation the penetration of a potential barrier becomes a random process specified by the penetration coefficient [23]. The energies of the escaping particles are distributed in a narrow range $|\varepsilon|/(k_B T) \sim 1 \ll \Delta V$ near the barrier top so that the potential (as in the classical case) can be approximated by the inverted parabola $V(x) \approx V_C - m\omega_C^2(x - x_C)^2/2$. The penetration coefficient through the parabolic potential barrier is given by Eq. (15), namely, $(1 + \exp[-2\pi\varepsilon/(\hbar\omega_C)])^{-1}$ [23]. The reflected particles on executing a cycle of the motion in the potential well will reproduce the distribution function $f(\varepsilon)$. By using the Green function (401) and the reflection coefficient $(1 + \exp[2\pi\varepsilon/(\hbar\omega_C)])^{-1}$, we obtain, using Melnikov's notation, the integral equation for $f(\varepsilon)$ [8]

$$f(\varepsilon) = \int_{-\infty}^{\infty} \frac{g(\varepsilon - \varepsilon')f(\varepsilon')}{1 + \exp(2\pi\varepsilon'/\hbar\omega_C)} d\varepsilon' \quad (409)$$

In order to solve Eq. (409) in a manner similar to the classical case, we write

$$f(\varepsilon) = \varphi(\varepsilon) [1 + \exp(2\pi\varepsilon/\hbar\omega_C)] \quad (410)$$

By substituting Eq. (410) into Eq. (409) and taking Fourier transforms via (407), we have in the λ domain

$$\varphi(\lambda) + \varphi(\lambda - i/y) = g(\lambda)\varphi(\lambda) \quad (411)$$

or

$$\varphi(\lambda - i/y) = -G(\lambda)\varphi(\lambda) \quad (412)$$

where $G(\lambda) = 1 - g(\lambda)$ and the quantum parameter is

$$y = \hbar\omega_C/(2\pi k_B T) \quad (413)$$

Equation (412) has to be solved subject to the boundary condition

$$\varphi(\lambda) = \frac{ik_B T}{\pi\hbar(\lambda + i)} \sinh\left(\frac{\hbar\omega_A}{2k_B T}\right) e^{-\Delta V}, \quad |\lambda + i| \ll 1 \quad (414)$$

which follows from the normalized distribution function for the harmonic potential in the vicinity of the well bottom that is (cf. our Introduction)

$$f(\varepsilon) \approx \frac{e^{-\Delta V - \varepsilon/(k_B T)}}{2\pi\hbar \sum_{n=0}^{\infty} e^{-\hbar\omega_A(n+1/2)/(k_B T)}} = \frac{\sinh[\hbar\omega_A/(2k_B T)]}{\pi\hbar} e^{-\Delta V - \varepsilon/(k_B T)} \quad (415)$$

In order to solve Eq. (412), we must factorize $G(\lambda)$ into a product of the functions $G^\pm(\lambda)$ according to Eqs. (111) and (112).

Now by introducing the auxiliary function

$$\psi(\lambda) = \frac{1}{G^-(\lambda)} \prod_{n=1}^{\infty} \frac{G^+(\lambda + in/y)}{G^-(\lambda - in/y)} \quad (416)$$

we see by direct substitution that it satisfies the relation

$$\psi(\lambda - i/y) = G(\lambda)\psi(\lambda) \quad (417)$$

Then by substituting Cauchy's integral representation of $G(\lambda)$ Eq. (111) into Eq. (416) and performing the summation, we have

$$\begin{aligned} \psi(\lambda) &= \exp \left[\frac{1}{2\pi i} \int_{-\infty}^{\infty} \left\{ \frac{1}{\lambda' - \lambda} + 2 \sum_{n=1}^{\infty} \left(\frac{\lambda' - \lambda}{(\lambda' - \lambda)^2 - (in/y)^2} \right) \right\} \ln G(\lambda') d\lambda' \right] \\ &= \exp \left[\frac{y}{2i} \int_{-\infty}^{\infty} \frac{\ln G(\lambda')}{\tanh [y(\lambda' - \lambda)]} d\lambda' \right] \end{aligned} \quad (418)$$

Comparison of Eqs. (412), (417), and (415) shows that $\varphi(\lambda)$ differs from the auxiliary function $\psi(\lambda)$ only by a function that changes its sign upon shifting its argument by in/y and has a pole at $\lambda = -i$. It is obvious that this function is simply given by $1/\sinh [\pi y(\lambda + i)]$. Thus, the solution of Eq. (412) with the boundary condition (414) is given in terms of the auxiliary function by

$$\varphi(\lambda) = \frac{i\omega_C}{2\pi} \frac{\psi(\lambda)}{\psi(-i)} \frac{\sinh [\hbar\omega_A/(2k_B T)]}{\sinh [\hbar\omega_C(\lambda + i)/(2k_B T)]} e^{-\Delta V} \quad (419)$$

5. Escape Rate in the Underdamped Quantum Region

Now we also saw in our Introduction that the lifetime τ of a Brownian particle in a deep potential well can be expressed via Eq. (12) [8]. However, like the classical case, the TST Eq. (12) in the quantum case applies only in the intermediate damping regime and so does not explicitly contain any dependence on the friction. Thus,

in the *underdamped* regime, Eq. (12) must again be modified by introducing the depopulation factor, namely, A so that

$$\tau^{-1} = A(\Delta, y) \frac{\omega_C \sinh[\hbar\omega_A/(2k_B T)]}{2\pi \sin[\hbar\omega_C/(2k_B T)]} e^{-\Delta V} \quad (420)$$

In the quantum case the depopulation factor $A(\Delta, y)$ takes into account the interaction of the Brownian particle with the heat bath via the dissipation parameter Δ and also includes the high-temperature quantum tunneling effects near the top of the barrier via the quantum parameter y .

Now we know that as far as quantum effects are concerned only those particles that penetrate the classically opaque potential barrier via tunneling contribute to the escape rate so that the rate is given by the following equation involving the penetration coefficient [cf. Eq. (15) with $V_C = 0$] [8]

$$\tau^{-1} = \int_{-\infty}^{\infty} \frac{f(\varepsilon) d\varepsilon}{1 + \exp(-2\pi\varepsilon/\hbar\omega_C)} = \int_{-\infty}^{\infty} \varphi(\varepsilon) e^{2\pi\varepsilon/\hbar\omega_C} d\varepsilon = \varphi(-i/y) \quad (421)$$

From Eqs. (418)–(421), we then have the general expression for A valid in the *underdamped* regime

$$\begin{aligned} A(\Delta, y) &= \exp \left[\frac{y}{2i} \int_{-\infty}^{\infty} \ln G(\lambda') \left\{ \frac{1}{\tanh[\pi(y\lambda' + i)]} - \frac{1}{\tanh[\pi y(\lambda' + i)]} \right\} d\lambda' \right] \\ &= \exp \left[\int_{-\infty}^{\infty} \frac{y \sin(\pi y)}{\cosh[2\pi y(\lambda' + i/2)] - \cos(\pi y)} \right. \\ &\quad \left. \times \ln [1 - \exp\{w(\lambda') - w(0)\}] d\lambda' \right] \\ &= \exp \left[\int_{-\infty}^{\infty} \frac{y \sin(\pi y) \ln [1 - e^{-\Delta R(\lambda, y)}]}{\cosh(2\pi y \lambda) - \cos(\pi y)} d\lambda \right] \end{aligned} \quad (422)$$

Here, we have written $\Delta R(\lambda, y) = w(0) - w(\lambda - i/2)$, where $w(\lambda)$ is the Fourier transform of the quantum transition probability in the first order of perturbation theory $w(\varepsilon)$ given by Eq. (405) that replaces the classical argument $\Delta(\lambda^2 + 1/4)$ from Eq. (119).

In the extremely undamped regime ($\Delta \ll 1$), the inner exponent in Eq. (422) can be expanded yielding

$$A(\Delta, y) \approx \exp \left\{ \int_{-\infty}^{\infty} \frac{y \sin \pi y (\ln [R(\lambda, y)] + \ln \Delta)}{\cosh 2\pi\lambda y - \cos \pi y} d\lambda \right\} = a(y) \Delta^{-\infty} \int_{-\infty}^{\infty} \frac{y \sin \pi y}{\cosh 2\pi\lambda y - \cos \pi y} d\lambda \quad (423)$$

where

$$a(y) = \exp \left\{ \int_{-\infty}^{\infty} \frac{y \sin \pi y \ln R(\lambda, y)}{\cosh 2\pi\lambda y - \cos \pi y} d\lambda \right\} \quad (424)$$

In order to evaluate the integral occurring in the exponent of Eq. (423), we write $y = 1 - z$ so that

$$\begin{aligned} \frac{y \sin \pi y}{\cosh 2\pi\lambda y - \cos \pi y} &= \frac{(1 - z) \sin \pi(1 - z)}{\cosh 2\pi\lambda(1 - z) - \cos \pi(1 - z)} \\ &\approx \frac{\pi z}{1 + \cosh 2\pi\lambda} + \frac{\pi z^2 (2\pi\lambda \sinh 2\pi\lambda - \cos 2\pi\lambda - 1)}{(1 + \cosh 2\pi\lambda)^3} + o(z^3) \end{aligned}$$

Now since

$$\begin{aligned} \int_{-\infty}^{\infty} \frac{\pi z}{1 + \cosh 2\pi\lambda} d\lambda &= z \\ \int_{-\infty}^{\infty} \frac{\pi z^2 (2\pi\lambda \sinh 2\pi\lambda - \cos 2\pi\lambda - 1)}{(1 + \cosh 2\pi\lambda)^3} d\lambda &= 0 \end{aligned}$$

We have ultimately the quantum VLD depopulation factor as a product of a purely quantum and a classical factor with quantum modifications, namely,

$$A(\Delta, y) \approx a(y) \Delta^z = a(y) \Delta^{1-y} = a(y) \Delta^{1-\hbar\omega_C/(2\pi k_B T)} \quad (425)$$

The condition of applicability is $y < 1$, that is, relatively high temperatures. The expression (425) shows that with decreasing temperature T , the contribution of quantum tunneling predominates over the effect of depletion of the distribution function. Therefore, the escape rate extrapolated to low temperatures $k_B T_0 = \hbar\omega_C/(2\pi)$ becomes *independent of dissipation*. For high temperatures ($k_B T \gg \hbar\omega_C$) Eq. (425) yields the classical VLD result $A \approx \Delta$.

We saw [Eq. (370)] that in the semiclassical approximation the matrix elements $\langle \varepsilon | \hat{x}(t) | \varepsilon' \rangle$ of a quantum transition from the state ε' to the state ε can be

expressed via the Fourier components of the classical trajectory $x(t)$ in Melnikov's notation

$$\langle \varepsilon | \hat{x}(t) | \varepsilon' \rangle = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} x(t) e^{i(\varepsilon - \varepsilon')t/\hbar} dt \quad (426)$$

Since the separatrix energy coincides with $\varepsilon = 0$, in order to evaluate the Fourier transform we need only the classical trajectory $x(t)$ corresponding to energy $\varepsilon = 0$. It is defined by the implicit relation

$$t(x) = \pm \int_{x_1}^x \frac{dx'}{\sqrt{-2V(x')/m}} \quad (427)$$

where x_1 is the classical turning point at $t = 0$ and the signs $+$ and $-$ correspond to positive and negative velocities of the particle, respectively. The particle starts from $x = 0$ at $t = -\infty$ and returns to this point for $t \rightarrow \infty$. Further progress and derivation of the expression for the quantum argument $R(\lambda, y)$ is only possible for *explicit* potentials $V(x)$. Here, we give examples of the calculation of the matrix elements $\langle \varepsilon | x(t) | \varepsilon' \rangle$ for cubic, double-well, and periodic potentials.

We commence with the cubic potential that is

$$V(x) = -\frac{1}{2}m\omega^2 x^2 \left(1 - \frac{x}{x_1}\right) \quad (428)$$

We have for this potential

$$t(x) = \frac{1}{\omega} \int_{x_1}^x \frac{dx'}{x' \sqrt{1 - x'/x_1}} = -\frac{2i}{\omega} \arccos \left(\sqrt{x/x_1} \right) \quad (429)$$

so that the classical trajectory is given by

$$x(t) = \frac{x_1}{\cosh^2(\omega t/2)} \quad (430)$$

The matrix elements $\langle \varepsilon | \hat{x}(t) | \varepsilon' \rangle$ for the cubic potential are then given, recalling Eq. (426), by the Fourier transform over the time variables in the classical trajectories

$$\langle \varepsilon | \hat{x}(t) | \varepsilon' \rangle = \frac{x_1}{2\pi\hbar} \int_{-\infty}^{\infty} \frac{e^{i(\varepsilon - \varepsilon')t/\hbar} dt}{\cosh^2(\omega t/2)} = \frac{2x_1(\varepsilon - \varepsilon')}{\hbar^2 \omega^2 \sinh[\pi(\varepsilon - \varepsilon')/\hbar\omega]} \quad (431)$$

The quantum transition (Golden Rule) probability is then recalling Eq. (405)

$$w(\varepsilon) = \frac{8\pi m \beta x_1^2 \varepsilon^3}{\hbar^5 \omega^4 \sinh^2[\pi \varepsilon / \hbar \omega]} (\coth[\varepsilon / (2k_B T)] - 1) \quad (432)$$

The Fourier transform of the quantum transition probability in the λ -domain, where we have shifted the argument as in the classical case is

$$\begin{aligned} w(\lambda - i/2) - w(0) &= \int_{-\infty}^{\infty} \frac{8\pi m \beta x_1^2 \varepsilon^3 (\coth[\varepsilon / (2k_B T)] - 1)}{\hbar^5 \omega^4 \sinh^2[\pi \varepsilon / \hbar \omega]} (e^{i(\lambda - i/2)\varepsilon / (k_B T)} - 1) d\varepsilon \\ &= \frac{8\beta \omega m x_1^2}{15k_B T} \int_{-\infty}^{\infty} \frac{15x^3 (\cosh x - \cosh 2\lambda x)}{2\pi^4 y^5 \sinh x \sinh^2[x/y]} dx = R(\lambda, y) \Delta \end{aligned} \quad (433)$$

where $y = \hbar \omega / 2\pi k_B T$, $x = \varepsilon / (2k_B T)$,

$$R(\lambda, y) = \frac{15}{2\pi^4 y^5} \int_{-\infty}^{\infty} \frac{x^3 (\cosh x - \cosh 2\lambda x)}{\sinh x \sinh^2[x/y]} dx \quad (434)$$

and the dissipation parameter is

$$\Delta = \left| \int_{x_1}^0 \sqrt{-2V(x')/m} dx' \right| = \frac{8\beta \omega m x_1^2}{15k_B T}$$

In like manner, we evaluate $R(\lambda, y)$ for a double-well potential that can be represented as

$$V(x) = -\frac{1}{2} m \omega^2 x^2 \left(1 - \frac{x^2}{x_1^2} \right) \quad (435)$$

Here, the trajectory is determined by

$$t(x) = \frac{1}{\omega} \int_{x_1}^x \frac{dx'}{x \sqrt{1 - x^2/x_1^2}} = -\frac{i}{\omega} \arccos(x/x_1) \quad (436)$$

that is,

$$x(t) = \frac{x_1}{\cosh(\omega t)} \quad (437)$$

The matrix elements $\langle \varepsilon | \hat{x}(t) | \varepsilon' \rangle$ for the double-well potential are then given by

$$\langle \varepsilon | \hat{x}(t) | \varepsilon' \rangle = \frac{x_1}{2\pi\hbar} \int_{-\infty}^{\infty} \frac{e^{i(\varepsilon-\varepsilon')t/\hbar} dt}{\cosh(\omega t)} = \frac{x_1}{2\hbar\omega \cosh[\pi(\varepsilon - \varepsilon')/2\hbar\omega]} \quad (438)$$

Thus, the quantum transition probability in this case is

$$w(\varepsilon) = \frac{\pi m \beta x_1^2 \varepsilon}{2\hbar^3 \omega^2 \cosh^2[\pi\varepsilon/2\hbar\omega]} (\coth[\varepsilon/(2k_B T)] - 1) \quad (439)$$

so that

$$\begin{aligned} w(\lambda - i/2) - w(0) &= \int_{-\infty}^{\infty} w(\varepsilon) (e^{i(\lambda-i/2)\varepsilon/(k_B T)} - 1) d\varepsilon \\ &= \frac{2\omega\beta m x_1^2}{3k_B T} \int_{-\infty}^{\infty} \frac{3\pi x (\cosh yx - \cos 2\lambda yx)}{8y \sinh yx \cosh^2(\pi x/2)} dx = R(\lambda, y) \Delta \end{aligned} \quad (440)$$

where the dissipation parameter is

$$\Delta = \frac{2\beta}{k_B T} \int_0^{x_1} \sqrt{-2mV(x)} dx = \frac{2\beta\omega m x_1^2}{3k_B T}, \quad y = \hbar\omega/(2k_B T), \quad x = \varepsilon/(2yk_B T)$$

and the quantum argument is

$$R(\lambda, y) = \frac{3\pi}{8y} \int_{-\infty}^{\infty} \frac{x (\cosh yx - \cos 2\lambda yx)}{\sinh yx \cosh^2(\pi x/2)} dx \quad (441)$$

In the classical limit because

$$\lim_{\hbar \rightarrow 0} \frac{\cosh yx - \cos 2\lambda yx}{y \sinh(yx)} = \lim_{y \rightarrow 0} \frac{\cosh yx - \cos 2\lambda yx}{y \sinh(yx)} = \frac{x}{2} (1 + 4\lambda^2) \quad (442)$$

we have

$$\lim_{\hbar \rightarrow 0} R(\lambda, y) = \frac{3\pi}{4} \left(\lambda^2 + \frac{1}{4} \right) \int_{-\infty}^{\infty} \frac{x^2 dx}{\cosh^2(\pi x/2)} = \lambda^2 + \frac{1}{4} \quad (443)$$

which is the (canonical) classical form. The foregoing classical expression has been used by Hänggi et al. [2] to simplify calculation of quantum escape rates.

In like manner for the periodic potential

$$V(x) = \frac{m\omega^2 x_1^2}{2\pi^2} \cos^2(\pi x/x_1) \quad (444)$$

we obtain

$$x(t) = \frac{2x_1}{\pi} \arctan(e^{\omega t}) \quad (445)$$

and

$$\langle \varepsilon | \hat{x}(t) | \varepsilon' \rangle = \frac{x_1}{\pi^2 \hbar} \int_{-\infty}^{\infty} \arctan(e^{\omega t}) e^{i(\varepsilon - \varepsilon')t/\hbar} dt = \frac{ix_1}{2(\varepsilon - \varepsilon') \cosh[\pi(\varepsilon - \varepsilon')/(2\hbar\omega)]} \quad (446)$$

$$R(\lambda, y) = \frac{1}{8y} \int_{-\infty}^{\infty} \frac{\cosh x - \cos(2\lambda x)}{x \sinh x \cosh^2[x/(2y)]} dx \quad (447)$$

The detailed calculation of the argument $R(\lambda, y)$ for this periodic potential and others is given in Ref. [8].

B. Translational Motion of a Quantum Brownian Particle in a Double-Well Potential

1. Master Equation in Phase Space and its Solution

We saw that dissipation and fluctuation of an assembly of particles in a potential under the influence of a heat bath is very often modeled [14,16] by the Brownian motion that is a particular *Stosszahlansatz* (essentially collisions are frequent but weak) for the Boltzmann equation describing the time evolution of the single-particle distribution function in phase space. Moreover, we also saw that the Brownian motion in a potential is ubiquitous in physics and chemistry, particularly to do with the nature of metastable states and the rates at which these states decay. Typical examples are current–voltage characteristics of Josephson junctions, the rate of condensation of a supersaturated vapor, dielectric and Kerr-effect relaxation in liquids and nematic liquid crystals, dynamic light scattering, chemical reaction rate theory in condensed phases, superparamagnetic relaxation, polymer dynamics, nuclear fission and fusion, and so on [2,13,14,155]. Now the classical theory of the Brownian motion is well established and is based either on the Langevin equation for evolution of the state vector [14] or on its accompanying Fokker–Planck equation [16]. However, we saw that a theory of dissipation based on the classical Brownian motion is often inadequate particularly at low temperatures because it ignores quantum effects. Quantum noise arising from quantum fluctuations is

also important in nanoscale and biological systems. We mention [155] the noise-assisted tunneling and transfer of electrons and quasiparticles. The characteristics of such quantum noise vary strongly with temperature and at high temperatures a crossover to Johnson–Nyquist noise essentially governed by the classical Brownian motion takes place. Yet another aspect of the subject that has come to the forefront in recent years is the quantum mechanics of macroscopic quantum variables such as the decay of a zero voltage state in a biased Josephson junction, flux quantum transitions in a SQUID [2], and the possible reversal by quantum tunneling, of the magnetization of a single-domain ferromagnetic particle. All these considerations necessitate a theory of quantum Brownian motion particularly one that addresses directly the issue of the quantum–classical correspondence [156] via a quantum analog of the classical Fokker–Planck equation. Such an evolution equation will allow dynamical parameters such as escape rates, correlation times, susceptibilities, and so on, to be calculated from the eigensolutions of that equation in a manner analogous to those of the Fokker–Planck equation. The availability of a master equation is a crucial factor for the purposes of this chapter because it then becomes possible to compare asymptotic solutions for parameters such as escape rates yielded by reaction rate theory with those calculated from such an equation.

If one wishes to include quantum effects in a diffusion equation treatment, however, a difficulty immediately arises, namely, one cannot speak, because of the uncertainty principle [139,157], of a particle having simultaneously a well-defined position and momentum, that is, the concept of a sharp phase point has no meaning in the quantum world. Therefore, one cannot define as in classical statistical mechanics a probability that the particle has a *particular position* and a *particular momentum*. Hence, one cannot define a true phase space probability distribution for a quantum mechanical particle. Nevertheless, functions bearing some resemblance to phase space distribution functions namely *quasiprobability distribution functions* have proven [139,157–160] very useful in quantum mechanical systems as they provide insights into the connection between classical and quantum mechanics allowing one to express quantum mechanical averages in a form that is very similar to that of classical averages. Thus, they are ideally suited to the study of the quantum–classical correspondence.

The description of quantum mechanics via phase space distributions advanced by Wigner [139] is an ideal starting point for the formulation of semiclassical quantum master equations. The Wigner phase space formalism [139,157] in quantum mechanics allows one to employ tools of classical physics in the quantum realm. For *closed* quantum systems, the time behavior of the Wigner function is governed by an evolution equation equivalent to the Schrödinger equation, which in the limit $\hbar \rightarrow 0$ becomes Liouville’s equation for the phase space distribution function in classical mechanics. Therefore, the Wigner formalism provides a natural quantum–classical connection.

We should remark that the quantum Brownian motion in a potential may also be treated using many other methods such as numerical simulations [46,54,161,162], the reduced density matrix [163,164], path integrals [165], and so on. In general, these permit a deep understanding of the dynamics of dissipative quantum systems. Moreover, many problems concerning quantum effects on diffusive transport properties, activated barrier crossing, and so on, have been solved. However, in spite of the progress achieved such methods possess certain practical disadvantages. For example, a simple time evolution equation for the reduced density matrix does not exist [22]. Moreover, path integrals have been usually confined to harmonic oscillator models since in general it is difficult or indeed impossible to evaluate them for any other potentials [165]. In spite of the formal power of numerical simulation methods, yielding numerically exact solutions, the understanding and interpretation of the qualitative behavior of the relevant physical quantities, is sometimes not at all obvious from them. One would, therefore, essentially expect that only a combined use of the latter complementary approaches may yield a comprehensive understanding of the quantum dynamics of the Brownian particle in a potential.

Hitherto little in the nature of detailed solutions of semiclassical master equations for the quantum phase space distribution functions describing quantum Brownian motion in an arbitrary external potential $V(x)$ has appeared in the literature (see, e.g., Refs [166–168]) hindering investigations of the range of validity of asymptotic expressions for escape rates, and so on, based on, for example, the turnover formula. In fact theoretical developments have usually been undertaken only for a quantum Brownian harmonic oscillator as treated by Agarwal [169] and others (see, e.g., Refs [170–173] and references cited therein). However, recently García-Palacios and Zueco [137,138] have proposed an effective method of solving the master equation for the quantum Brownian motion in an anharmonic potential $V(x)$. Their ideas suggest how Brinkman’s representation of the classical Fokker–Planck equation as a partial differential–recurrence relation in configuration space [33] and its associated solution methods based on matrix continued fractions via a suitable spatial basis for the observables [14,16] could be naturally extended to the quantum regime.

Inspired by these ideas, we have recently proposed a quantum master equation for the Brownian motion of a particle in a potential $V(x)$ [174,175]. Specifically we have demonstrated how the Wigner stationary distribution for closed systems can be used to *formally* establish a semiclassical master equation allowing one to study the quantum–classical correspondence. The dissipative barrier-crossing process is characterized by the (Kramers) escape rate Γ and by the quantum Mel’nikov turnover formula. In the classical case, Mel’nikov’s turnover formula has been exhaustively verified for the double-well potential by calculating the smallest nonvanishing eigenvalue of the Klein–Kramers equation for the phase space distribution function $W(x, p, t)$ by continued fraction methods [114,122,123,176]. The quantum Mel’nikov turnover formula for the double-well potential has also been tested

by a comparison with numerical simulation results for quantum rate constants by Topaler and Makri [46,161] (by using the path integral approach) and Barik et al. [177] (by solving numerically the quantum Langevin equation), the latter being based on the Wigner phase space distribution function.

Proceeding we now consider the semiclassical master equation for the quantum Brownian dynamics in the double-well potential. Specifically we shall apply the matrix continued fraction method of Voigtlaender and Risken [122] and Coffey et al. [123] (developed for the solution of the corresponding classical problem) to ascertain how quantum effects modify the behavior of the quantum equilibrium position correlation function $C(t) = k_B T \langle \int_0^{(k_B T)^{-1}} \hat{x}(-i\lambda\hbar) \hat{x}(t) d\lambda \rangle_0$, its spectrum, and correlation time, which essentially yields the escape rate. Here, the symbol $\langle \rangle_0$ denotes the equilibrium ensemble averages. This calculation will illustrate how to evaluate observables in the familiar classical manner. Moreover, the continued fraction results for the damping dependence of the quantum escape rate Γ will be compared with those yielded by the Mel'nikov quantum turnover equation for Γ so that the range of validity of the semiclassical master equation approach may be ascertained.

Now Wigner [139] showed that quantum mechanics can be reformulated using a phase space (x, p) quasiprobability distribution function

$$W(x, p, t) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \rho \left(x + \frac{1}{2}y, x - \frac{1}{2}y \right) e^{-ipy/\hbar} dy$$

where $\rho(x, x') = \langle x | \hat{\rho} | x' \rangle$ is the density matrix. Thus, the Wigner distribution function establishes a connection between the density matrix and a quasiprobability distribution in classical phase space. Moreover, one can calculate all quantum mechanical averages by pure c -number procedures, that is, by evaluation of averages just as in classical statistical mechanics. A detailed discussion of Wigner distribution functions is given in Refs [157–160].

Now the semiclassical master equation for the translational Brownian motion of a particle in a potential $V(x)$ based on Wigner's phase space formulation can be derived postulating a truncated Kramers–Moyal expansion by proceeding to the high-temperature limit and using the approximation of frequency independent damping, the resulting equation to order \hbar^2 is [20,174,175]

$$\begin{aligned} & \frac{\partial}{\partial t} W + \frac{p}{m} \frac{\partial W}{\partial x} - \frac{\partial V}{\partial x} \frac{\partial W}{\partial p} + \frac{\hbar^2}{24} \frac{\partial^3 V}{\partial x^3} \frac{\partial^3 W}{\partial p^3} + \dots \\ & = \beta \frac{\partial}{\partial p} \left[pW + k_B T m \left\{ 1 + \frac{\hbar^2}{12m(k_B T)^2} \frac{\partial^2 V}{\partial x^2} + \dots \right\} \frac{\partial W}{\partial p} \right] \end{aligned} \quad (448)$$

where m is the mass of the particle, β is a friction parameter measuring the strength of the coupling to the heat bath. The left-hand side of Eq. (448) is the quantum analog of the classical Liouville equation for the closed system while the right-hand side accounts for effects due to the coupling to the bath, that is, dissipation and fluctuations being the analog of the collision kernel (*Stosszahlansatz*) in kinetic theory. Equation (448) is a partial differential equation for the evolution of the quasiprobability distribution W in phase space akin to the Fokker–Planck equation immediately suggesting how the familiar powerful computational techniques developed for that equation [16] may be extended to the quantum domain as we have previously demonstrated for a cosine periodic potential [20]. The master equation (448) is written down explicitly to $o(\hbar^2)$ and higher order quantum correction terms to it may be calculated in like manner [20,171,175]. For example, the explicit form of the master equation up to $o(\hbar^4)$ is given in Refs [20,174,175]. That equation can be given, in principle, to any desired degree r of \hbar^{2r} .

We recall in passing that the corresponding master equation for the quantum Brownian oscillator in the weak coupling limit, $\hbar\beta/(k_B T) \ll 1$, originally studied by Agarwal [20,169] is

$$\frac{\partial W}{\partial t} + \frac{p}{m} \frac{\partial W}{\partial x} - m\omega_0^2 x \frac{\partial W}{\partial p} = \beta \frac{\partial}{\partial p} \left[pW + \langle p^2 \rangle_0 \frac{\partial W}{\partial p} \right] \quad (449)$$

where ω_0 is the oscillator frequency and $\langle p^2 \rangle_0 = (m\hbar\omega_0/2)\coth[\hbar\omega_0/(2k_B T)]$. Now Eq. (449) has the same mathematical form as the Fokker–Planck equation for a classical Brownian oscillator [16]; however, the diffusion coefficient $D_{pp} = \beta\langle p^2 \rangle_0$ is altered so as to include the quantum effects. This simple result essentially arises because the dynamical equation for the Wigner function for a quadratic Hamiltonian $\hat{H} = \hat{p}^2/2m + m\omega_0^2 \hat{x}^2/2$ in the absence of dissipation ($\beta = 0$) coincides with the corresponding classical Liouville equation [20].

In order to solve the master equation for the double-well potential given by Eq. (211) (which is accomplished following Wigner by perturbation theory in \hbar^2 with the perturbation expansion truncated at the terms linear in \hbar^2), we begin by introducing dimensionless variables as in the classical model [123]

$$x' = \frac{x}{\sqrt{\langle x^2 \rangle_0^{\text{cl}}}}, \quad p' = \frac{\eta p}{m\sqrt{\langle x^2 \rangle_0^{\text{cl}}}}, \quad t' = t/\eta, \quad \Lambda = \frac{\hbar^2}{48(\eta k_B T)^2}$$

$$\beta' = \eta\beta, \quad V(x') = Ax'^2 + Bx'^4, \quad A = \frac{a\langle x^2 \rangle_0^{\text{cl}}}{2k_B T}, \quad B = \frac{b(\langle x^2 \rangle_0^{\text{cl}})^2}{4k_B T}$$

where $\eta = \sqrt{m\langle x^2 \rangle_0^{\text{cl}}/(2k_B T)}$ is a characteristic time and $\langle x^2 \rangle_0^{\text{cl}}$ is the classical value ($\hbar \rightarrow 0$) of the mean squared displacement. For $A > 0$ and $B > 0$, the potential

$V(x')$ has only one minimum. For $A < 0$ and $B > 0$ (which is the case of interest, that is, distinct double wells), the potential $V(x')$ has two minima separated by a maximum at $x' = 0$ with potential barrier $\Delta V = Q = A^2/4B$. The normalization condition $\langle x'^2 \rangle_0^{\text{cl}} = 1$ implies that the constants A and B are not independent and are related via Eq. (218) [14,114,123]. For $A < 0$ and $Q \gg 1$, $B \approx Q$ due to asymptotic properties of $D_v(z)$ [72]. Thus, Eq. (448) becomes

$$\begin{aligned} & \frac{\partial}{\partial t'} W + p' \frac{\partial W}{\partial x'} - \frac{1}{2} \frac{\partial W}{\partial p'} \frac{\partial V}{\partial x'} + \frac{\Lambda}{4} \frac{\partial^3 W}{\partial p'^3} \frac{\partial^3 V}{\partial x'^3} \\ & = \beta' \frac{\partial}{\partial p'} \left\{ p' W + \left[\frac{1}{2} + \Lambda \frac{\partial^2 V}{\partial x'^2} \right] \frac{\partial W}{\partial p'} \right\} + \dots \end{aligned} \quad (450)$$

The stationary solution of Eq. (450) is the equilibrium Wigner distribution function $W_{\text{st}}^0(x', p')$ restricted to the term linear in the quantum parameter Λ and given by [139,174,175]

$$W_{\text{st}}^0(x', p') = \frac{e^{-p'^2 - V(x')}}{\sqrt{\pi} Z} \left\{ 1 + \Lambda \left[\left(2p'^2 - 3 \right) \frac{\partial^2 V(x')}{\partial x'^2} + \left(\frac{\partial V(x')}{\partial x'} \right)^2 \right] + \dots \right\} \quad (451)$$

where Z is the partition function in accordance with our first-order perturbation *Ansatz* and is given by

$$Z = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_{\text{st}}^0(x', p') dx' dp' = Z_{\text{cl}} + \Lambda Z_1 + \dots$$

$Z_{\text{cl}} = \int_{-\infty}^{\infty} e^{-V(x')} dx'$ is the classical partition function in configuration space and

$$Z_1 = \int_{-\infty}^{\infty} \left[V'(x')^2 - 2V''(x') \right] e^{-V(x')} dx'$$

According to linear response theory [178], in order to calculate a position correlation function $C(t)$, one must evaluate the decay transient of the system of Brownian particles following instantaneous switch-off of an external field of small magnitude ε . Thus, when the field is suddenly switched off at time $t = 0$, we shall be interested in the relaxation of a system starting from an equilibrium state I with the potential $V(x') - \varepsilon x'$ and the distribution function $W_{\text{st}}^\varepsilon (t \leq 0)$ to a new equilibrium state II with the potential $V(x')$ and the distribution function $W_{\text{st}}^0 (t \rightarrow \infty)$ given by Eq. (451). In linear response, the distribution function $W_{\text{st}}^\varepsilon$ is given by

$$W_{\text{st}}^\varepsilon(x', p') = W_{\text{st}}^0(x', p') + \varepsilon W_1^0(x', p') + \dots \quad (452)$$

where

$$W_1^0(x', p') = x' W_{\text{st}}^0(x', p') - 2\Lambda \frac{e^{-p'^2 - V(x')}}{\sqrt{\pi} Z_{\text{cl}}} \frac{\partial}{\partial x'} V(x') + \dots \quad (453)$$

Note that the transient response so formulated is truly *linear* because the change in amplitude ε of the external field is assumed to be very small, $\varepsilon \rightarrow 0$. Hence, we seek a general solution of Eq. (450) in the form

$$W(x', p', t') = W_{\text{st}}^0(x', p') + \varepsilon W_1(x', p', t') + \dots \quad (454)$$

where $W_1(x', p', t')$ can be represented as the Fourier series just as the classical case [122,123]

$$W_1(x', p', t') = \kappa e^{-p'^2 - [\kappa^2 x'^2 + V(x')]/2} \sum_{n=0}^{\infty} \sum_{q=0}^{\infty} \frac{H_q(\kappa x') H_n(p')}{\pi \sqrt{2^{n+q} n! q!}} c_{n,q}(t') \quad (455)$$

$\kappa = \alpha B^{1/4}$, and α is a scaling factor chosen to ensure optimum convergence of the continued fractions involved as suggested by Voigtlaender and Risken [122] (all results for the observables are independent of α). The initial condition for $W(x', p', t')$ at $t' = 0$ is $W(x', p', 0) = W_{\text{st}}^\varepsilon(x', p')$, which in linear response becomes

$$W_1(x', p', 0) = W_1^0(x', p') \quad (456)$$

By substituting Eq. (454) into Eq. (450), we have the differential–recurrence relations for the Fourier coefficients $c_{n,q}(t')$

$$\begin{aligned} & \frac{d}{dt'} c_{n,q}(t') + \gamma' \left[n c_{n,q}(t') - \Lambda \sqrt{n(n-1)} \right. \\ & \quad \left. \times (h_{q-2} c_{n-2,q-2} + g_q c_{n-2,q} + h_q c_{n-2,q+2}) \right] \\ & = \sqrt{n+1} \left[e_q c_{n+1,q+3}(t') + d_q^- c_{n+1,q+1}(t') \right. \\ & \quad \left. + d_{q-1}^+ c_{n+1,q-1}(t') + e_{q-3} c_{n+1,q-3}(t') \right] \\ & \quad - \sqrt{n} \left[e_q c_{n-1,q+3}(t') + d_q^+ c_{n-1,q+1}(t') \right. \\ & \quad \left. + d_{q-1}^- c_{n-1,q-1}(t') + e_{q-3} c_{n-1,q-3}(t') \right] \\ & \quad + \Lambda \sqrt{n(n-1)(n-2)} [f_{q-1} c_{n-3,q-1} + f_q c_{n-3,q+1}] \end{aligned} \quad (457)$$

where all the coefficients d_p^\pm , e_q , f_q , g_q , h_q are defined in Appendix B.4. Now Eq. (457) reduces by first-order perturbation treatment in Λ to a matrix three-term

differential–recurrence relation forced by the quantum term. Thus, by invoking the familiar general matrix continued fraction method for solving classical recurrence relations generated by the Fokker–Planck equation [14,16], we have in like manner the solution of the quantum differential–recurrence equation (457) (details of this solution are given in Appendix B.4).

2. Calculation of Observables

We recall now that the expectation value of a quantum operator \hat{Q} may be calculated using the Wigner function $W(x, p, t)$ in conjunction with the corresponding classical variable (Weyl symbol) $Q(x, p)$ as [179]

$$\langle \hat{Q} \rangle (t) = \int W(x, p, t) Q(x, p) dx dp$$

Noting that x' corresponds to the operator \hat{x}' [179], we have the averaged displacement $\langle \hat{x}' \rangle (t')$ as

$$\langle \hat{x}' \rangle (t') = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} x' W(x', p', t') dx' dp' = \varepsilon \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} x' W_1(x', p', t') dx' dp' \quad (458)$$

By using the orthogonality properties of the Hermite polynomials, we have from Eqs. (455) and (458) $\langle \hat{x}' \rangle (t')$ in terms of the Fourier coefficients $c_{2q-1}(t)$

$$\langle \hat{x}' \rangle (t') = \varepsilon \frac{\alpha Z_{cl} B^{1/4}}{\sqrt{\pi}} \sum_{q=1}^{\infty} c_{0,2q-1}(0) c_{0,2q-1}(t) \quad (459)$$

According to linear response theory [178], $\langle \hat{x}' \rangle (t')$ is related to the linear response after-effect function $C(t) = k_B T \left\langle \int_0^{(k_B T)^{-1}} \hat{x}'(-i\lambda\hbar) \hat{x}'(t) d\lambda \right\rangle_0$ via

$$\langle \hat{x}' \rangle (t') = \varepsilon C(t) \quad (460)$$

This may be verified in the quantum case by independently calculating both the after-effect function and the autocorrelation function from the Fourier coefficients. As before the one-sided Fourier transform $\tilde{C}(\omega) = \int_0^{\infty} C(t) e^{-i\omega t} dt$, that is, the spectrum of the equilibrium correlation function $C(t)$ is related to the dynamic susceptibility $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$ via

$$\chi(\omega) = C(0) - i\omega \tilde{C}(\omega) \quad (461)$$

One may also determine the correlation time T_c , which is a global characteristic of the relaxation process involved and is defined as usual as the area under the curve of $C(t)/C(0)$, because [14]

$$T_c = \frac{1}{C(0)} \int_0^{\infty} C(t) dt = \frac{\tilde{C}(0)}{C(0)} \quad (462)$$

In the high-barrier limit ($Q \gg 1$), the correlation time T_c closely approximates the inverse Kramers escape rate, that is, the longest relaxation time for the double-well potential [16].

3. Mel'nikov's Turnover Formula for the Escape Rate

We saw in detail how Mel'nikov [8,9] extended his solution of the classical Kramers turnover problem to include quantum effects in a semiclassical way by deriving a (universal) formula valid for all values of damping for the quantum rate Γ_M above the crossover temperature between tunneling and thermal activation, namely,

$$\Gamma_M = \Upsilon \Gamma^{\text{IHD}} \quad (463)$$

Here, Υ is the quantum depopulation factor, Γ^{IHD} is the quantum escape rate for the double-well potential in the IHD region where $\beta' \geq 1$ and [137,138]

$$\Gamma^{\text{IHD}} = \Xi \Gamma_{\text{cl}}^{\text{IHD}} \quad (464)$$

Here, $\Gamma_{\text{cl}}^{\text{IHD}}$ is the classical IHD escape rate for the double-well potential given by [123]

$$\Gamma_{\text{cl}}^{\text{IHD}} = \frac{\Omega \omega_C}{\pi \omega_A} e^{\Delta V} \quad (465)$$

$\Delta V = Q$ is the normalized barrier height, $\omega_A = \sqrt{2} \eta^{-1} (QB)^{1/4}$ and $\omega_C = 2 \eta^{-1} (QB)^{1/4}$ are, respectively, the well and barrier angular frequencies, $\Omega = \eta^{-1} \left(\sqrt{\beta'^2/4 + \eta^2 \omega_A^2} - \beta'/2 \right)$ is the eigenvalue associated with the unstable barrier-crossing mode, and the quantum correction factor Ξ is given by Eq. (13).

The quantum depopulation factor Υ for a symmetrical double-well potential can be written as [8,9]

$$\Upsilon(\Delta, y) = \frac{A^2(\Delta, y)}{A(2\Delta, y)} \quad (466)$$

Here, A is the quantum depopulation factor for a single well, $y = 2\sqrt{6\Lambda\sqrt{QB}}$ is a dimensionless parameter, depending on the ratio of the quantum parameter

Λ to the barrier height parameter, and Δ is the loss parameter as defined in the Introduction, namely,

$$\Delta = \frac{\beta' S}{\eta k_B T} \quad (467)$$

where $S = \oint_{\text{well}} \sqrt{-2mV(x)} dx$ is the action associated with the path along the top of barrier given by

$$S = 2 \int_0^{x_1} \sqrt{-2mV(x)} dx = \frac{8\sqrt{2}}{3} \eta k_B T \left(\frac{Q^3}{B} \right)^{1/4} \quad (468)$$

[$x_1 = \sqrt{-2a/b}$ is one of the roots of the equation $V(x) = 0$]. On this path, a particle starts with zero velocity at the top of the barrier and, having descended into the well, returns again to the top of the barrier. For $Q \gg 1$, $S \sim 8\eta k_B T \sqrt{2Q}/3$. The quantum depopulation factor for a single well $A(\Delta, y)$ is given by [8,9] (see Section III.A.5)

$$A(\Delta, y) = \exp \left\{ \frac{y \sin y}{\pi} \int_{-\infty}^{\infty} \frac{\ln[1 - e^{-\Delta R(\lambda, y)}] d\lambda}{\cosh(2y\lambda) - \cos y} \right\} \quad (469)$$

where $R(\lambda, y)$ is given by Eq. (441). Thus, one may evaluate the escape rate [from Eqs. (463)–(469) and Eq. (441), where $\omega = \sqrt{-a/m}$] that may then be compared with the semiclassical solution obtained from Eq. (457) using matrix continued fractions. It should be noted that the universal equation (463) for the escape rate can be used only for high barriers (say $Q \geq 3$) with, however, no limitation on the quantum parameter Λ .

4. Comparison of the Numerical and Analytical Approaches

In Figs. 25 and 26, we show the spectrum of $\text{Im}[\tilde{C}(\omega)]$ and $\text{Re}[\tilde{C}(\omega)]$ as calculated from the series of Fourier coefficients, Eq. (459), by the matrix continued fraction method for barrier height parameters $Q = 5$ and 10 and various values of $\beta' = 1, 10$, and 100. The low-frequency part of the spectra $\tilde{C}(\omega)$ is due to the slow overbarrier relaxation of the particles in the double-well potential. Just as the classical case [123], this low-frequency part may be approximated by a simple Lorentzian

$$\tilde{C}(\omega) \approx \frac{1}{\Gamma_M + i\omega} \quad (470)$$

where Γ_M is the escape rate rendered by Mel'nikov's universal quantum rate, Eq. (463). It is apparent from Figs. 25 and 26 that the simple Eq. (470) accurately describes the quantum effects in the relaxation phenomenon at low frequencies

Figure 25. The imaginary part of the spectrum $\tilde{C}(\omega)$ versus the normalized frequency $\eta\omega$ for various values of the damping parameter β' , quantum parameter $\Lambda=0$ (classical limit; dashed lines) and $\Lambda=0.004$ (solid lines), and barrier height $Q=5$ and $Q=10$. Solid and dashed lines are the continued fraction solution [Eq. (460)]. Open circles are the Lorentzian spectra [Eq. (470)] for $\Lambda=0.004$.

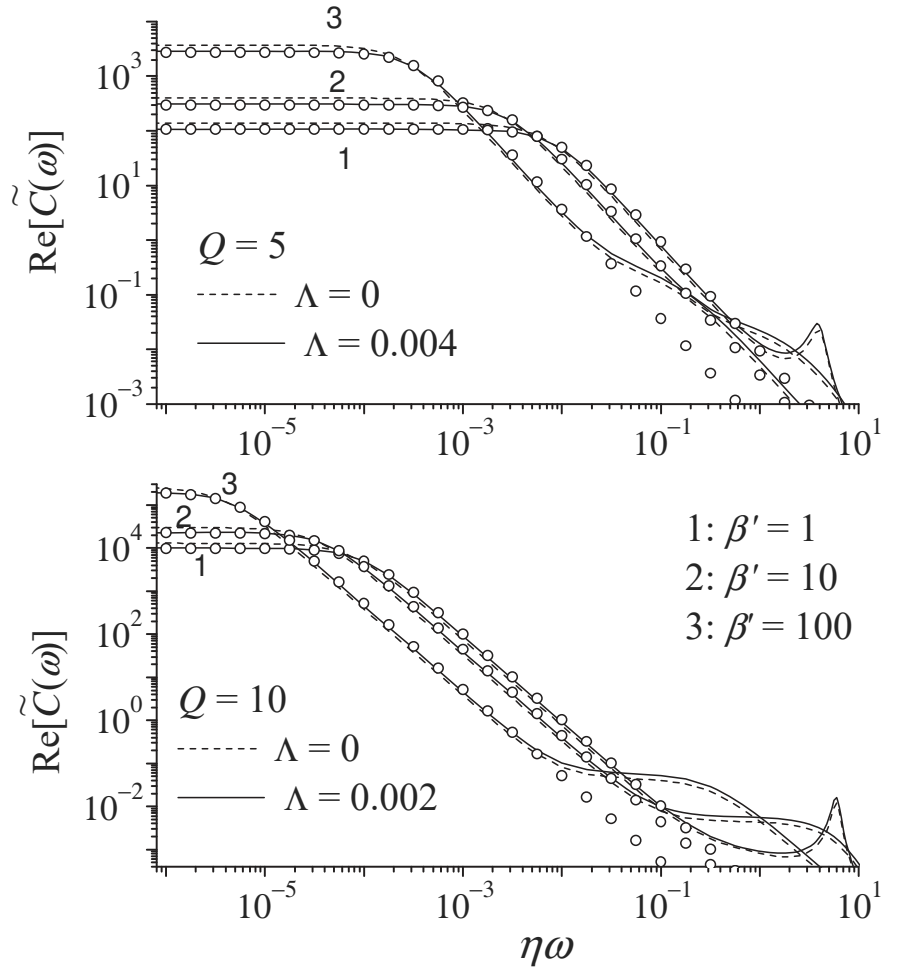
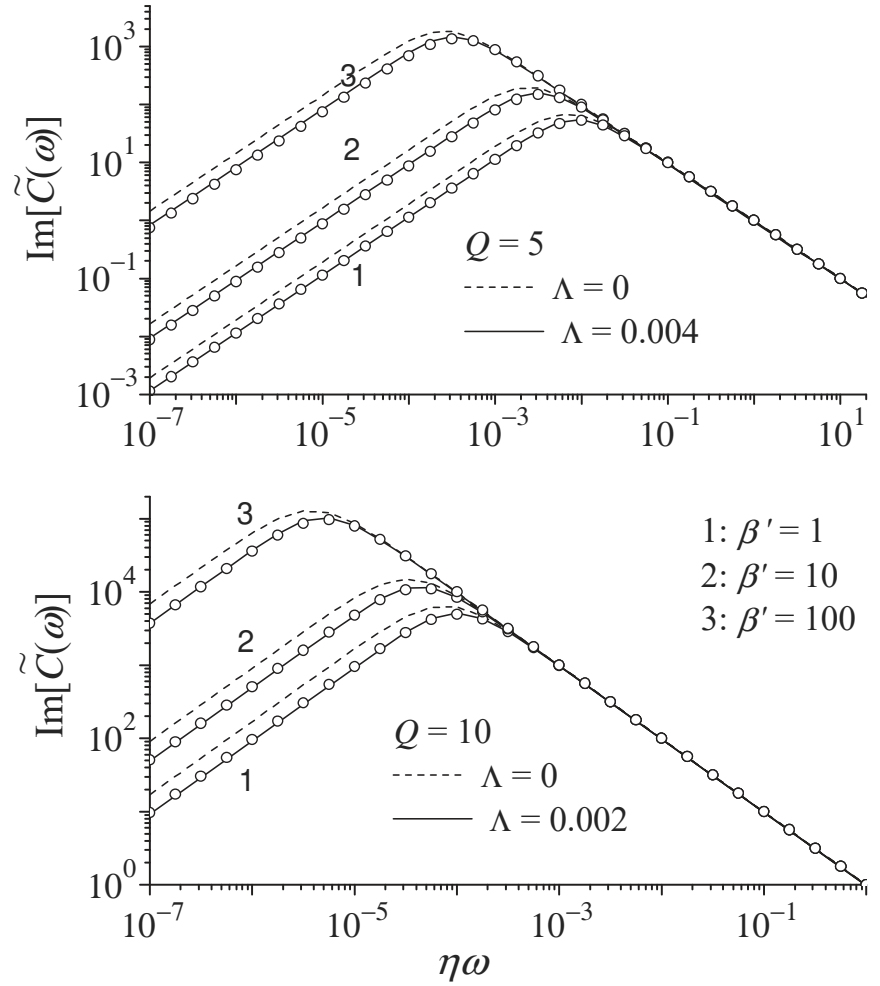


Figure 26. $\text{Re}[\tilde{C}(\omega)]$ versus $\eta\omega$ for various values of β' , Λ , and Q . Key as in Fig. 25.

($\omega \leq \Gamma_M$). It is also apparent from Fig. 25 particularly in the high-barrier case that tunneling near the top of the barrier increases the frequency of the maximum $\omega_R = \Gamma_M$ of the low-frequency peak in $\text{Im} [\tilde{C}(\omega)]$ and decreases the low-frequency side of $\text{Im} [\tilde{C}(\omega)]$; a phenomenon that can be ascribed to effective lowering of the potential barrier due to the tunneling that increases the escape rate as identified by Wigner [24]. Furthermore, the quantum effects decrease as the frequency increases above the peak frequency, where barrier crossing is no longer the dominant relaxation process. As far as the dependence of the low-frequency part of the spectrum is concerned, the frequency ω_R decreases as the damping parameter β' increases. For small damping ($\beta' < 0.1$), the frequency ω_R decreases with decreasing β' for given values of Q . A very high-frequency band is visible in the spectrum of $\text{Re}[\tilde{C}(\omega)]$ in Fig. 26 at moderate damping ($\beta' = 1$) due to the fast oscillations of the particles in the potential wells. For smaller damping, $\beta' \ll 1$, two sharp peaks appear in the high-frequency part of the spectra $\text{Re}[\tilde{C}(\omega)]$ signifying the existence of a family of peaks that occur just as in the classical case [123]. These peaks occur at the fundamental and second harmonic frequencies, and so on, of the almost free periodic motion of the particle in the double-well potential $V(x)$. We should remark that the description of the quantum effects in the high-frequency response in the double-well potential via the Wigner formalism applies only when the conditions $\eta \Delta E / \hbar \leq \beta'$, and $\Delta E / \hbar \leq \omega_A$ are satisfied. Here, ΔE is the energy difference between the two lowest energy levels in the potential well and $\omega_A \sim \sqrt{2} Q^{3/4} / \eta$ is the characteristic frequency of the nonlinear oscillator. Under these conditions, the discrete spectral lines corresponding to the transitions between the energy levels in the wells are indistinguishable in the spectrum $\text{Re}[\tilde{C}(\omega)]$. For moderate barriers, the inequality $\eta \Delta E / \hbar \leq \beta'$ breaks down only for very small damping. Moreover, the classical limit holds if the conditions $\Delta E / (k_B T) \ll 1$ and $\eta \Delta E / \hbar \ll \beta'$ are satisfied.

The longest relaxation time τ predicted by Mel'nikov's formula $\tau = \Gamma_M^{-1}$ [Eq. (463)] that we recall has been verified by computer simulation [46] and the relaxation time T_c / η from Eq. (462) calculated via matrix continued fractions is shown in Figs. 27 and 28 for barrier heights $Q = 5$ and 10, respectively, as a function of the (dimensionless) damping parameter β' characterizing the coupling to the heat bath. In relation to the matrix continued fraction calculations of the escape rate, we recall that the (normalized) time T_c / η being of exponential order accurately approximates the inverse escape rate for symmetrical potentials for all significant barrier heights. We further remark that the inverse of the universal quantum rate provides a reasonably good approximation to T_c / η for almost all β' values with a deviation of some of 20% for small friction β' and relatively low barriers, for example, $Q = 5$, as Λ increases. The agreement between the numerically calculated τ and the quantum rate result, however, improves as the barrier height increases (see Fig. 27). The results of the calculations suggest that in applying quantum rate theory to relatively low barriers that the theory should be modified to incorporate finite-barrier effects as in the classical case as envisaged by Mel'nikov [74]. In order

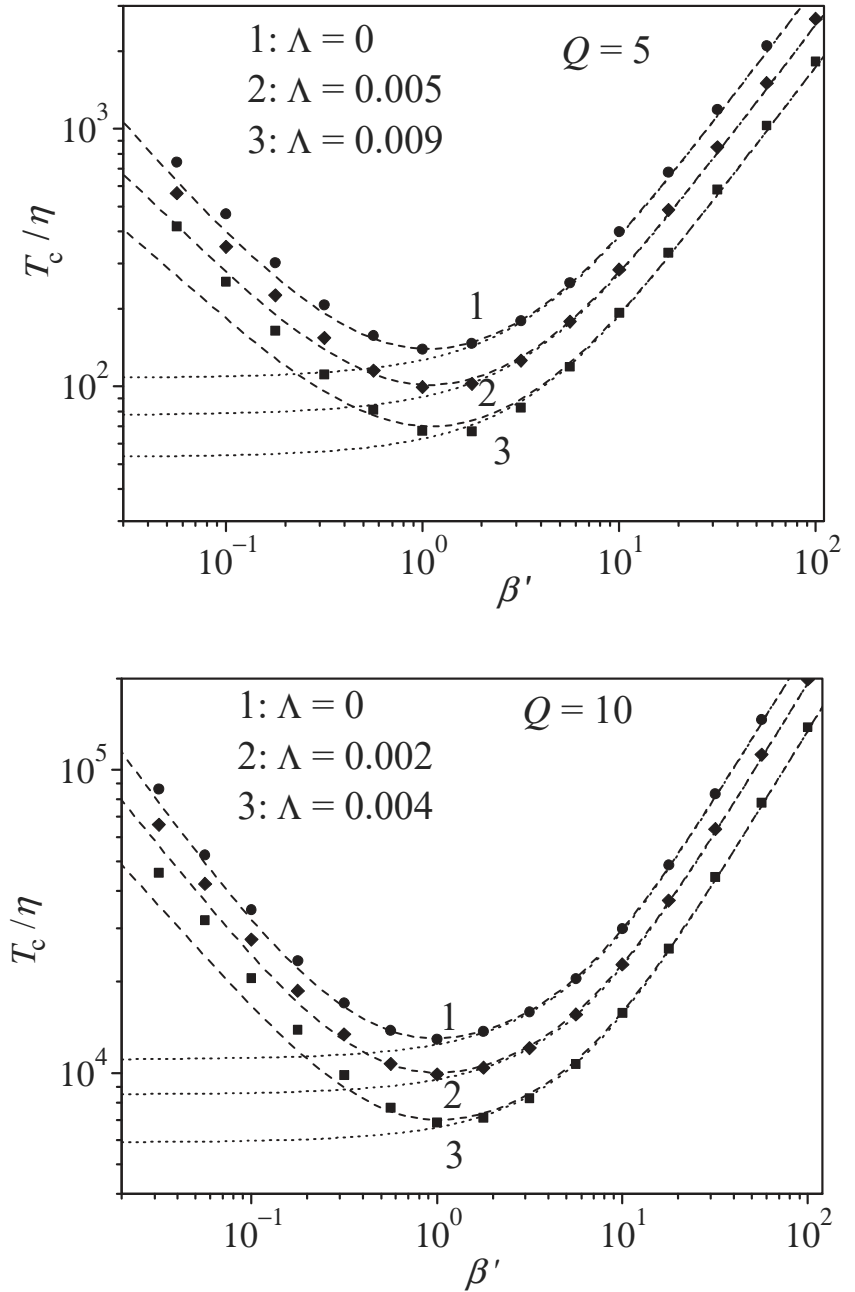


Figure 27. Correlation time T_c/η [Eq. (462), symbols] versus damping parameter β' as compared with the Mel'nikov–Meshkov formula [Eq. (463), dashed lines] for high barriers $Q=5$ and various values of the quantum parameter Λ . The IHD relaxation times $\tau_{\text{IHD}}/\eta = (\eta\Gamma^{\text{IHD}})^{-1}$ [Eq. (465), dotted lines] are also shown for comparison.

to improve the accuracy of the universal turnover formula, we have mentioned that Mel'nikov [74] suggested a systematic way of accounting for finite-barrier corrections. Analysis of the translational Brownian motion in a cosine potential demonstrates that if such corrections are included, the accuracy of the universal formula is considerably improved [51,75]. This method may also be applied here.

By way of further illustration, we show in Fig. 28 the correlation time T_c/η and the inverse of universal quantum rate $(\eta\Gamma_{\text{M}})^{-1}$ as functions of barrier height Q for large and small damping parameters $\beta' = 10$ and 0.1 , respectively. Clearly the correspondence between both results is very good for all relevant values of Q , for example, $Q > 3$. The discrepancy for $Q < 2$ arises simply because the assumption of a high barrier ($Q \gg 1$) is always used in the derivation of asymptotic escape rate formulas. The largest quantum effects obviously occur for the highest barriers

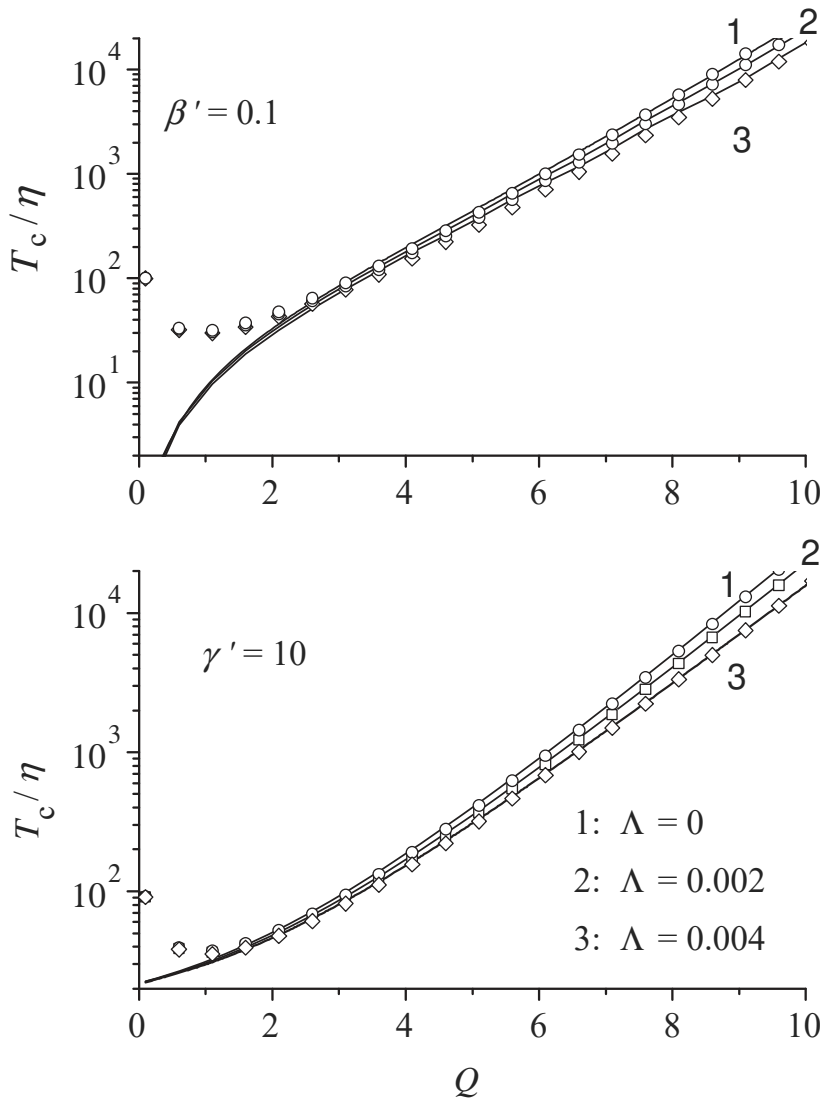


Figure 28. The correlation time T_c/η [matrix continued fraction solution, Eq. (462), solid lines] versus the barrier parameter Q for $\gamma' = 0.1$ (low damping) and $\beta' = 10$ (high damping) and various values of the quantum parameter Λ as compared with the Mel'nikov equation (463) (symbols).

as is obvious by inspection of Fig. 28. Moreover, they manifest themselves even for very small values of Λ .

In conclusion of this section, we have shown how quantum effects in the Brownian motion of a particle in a double-well potential may be studied using a semiclassical master equation based on the extension of Wigner's phase space formulation of quantum mechanics to an open system. Our treatment allows one to use all the solution techniques previously developed for the classical Fokker-Planck equation [14,16] rendering a transparent treatment of the quantum problem. Moreover, our results are in agreement with those of quantum reaction rate theory that constitutes a benchmark solution verified by quantum mechanical simulations [46,161,177]. The most significant manifestation of the quantum effects above the crossover temperature between tunneling and thermal activation appears to be in connection with the low-frequency relaxation via transitions across the potential barrier. In this frequency range, the relaxation process is accurately described by a single Lorentzian with relaxation time given by the inverse of Mel'nikov's universal quantum rate so providing a very simple picture of the quantum relaxation.

Our matrix continued fraction solution is valid only for small values of the quantum parameter Λ ($\Lambda \ll 1$) as in our perturbation procedure we have neglected all terms of the order of Λ^2 and higher. In order to improve the accuracy of matrix continued fraction calculations for larger values of Λ , additional terms of the order of Λ^2 , and so on, should be included in the master equation (448). These higher order quantum correction terms to the master equation, may be calculated, in principle, to any desired degree r of \hbar^{2r} [174,175]. Finally, we should remark in the context of our semiclassical solution that hitherto the quantum Brownian motion in a double-well potential has usually been treated only by means of numerical simulations (see, e.g., Refs [46,161,168,177,180]). These methods in general allow one to understand quantum effects on diffusive transport properties, activated barrier crossing, and so on. However, in spite of their great power they possess certain practical disadvantages because the qualitative behavior of the simulated physical quantities, is not always obvious from them. In general, therefore, one may expect that only a combined use of the complementary approaches of numerical simulation and the analytical methods described here is capable of yielding a comprehensive understanding of the quantum Brownian dynamics in a potential.

C. Translational Motion of a Quantum Brownian Particle in a Periodic Potential

1. Solution of the Master Equation in Phase Space

Here, we show how to solve the master equation for a quantum particle moving in the periodic potential

$$V(x) = -V_0 \cos(x/x_0) \quad (471)$$

where x is the position of the particle and x_0 is a characteristic length. Both the classical and the quantum Brownian motion in periodic potentials have been used, for example, to model the diffusion in solids, premelting films, and surfaces (see, e.g., Refs [54,181,182]). Furthermore, Brownian motion in periodic potentials arises in a number of other important physical applications (see Section II.G).

Now we saw that the analytical approaches to the problem are based on Kramers escape rate theory [15]. However, we recall that the Kramers escape rate problem in a periodic potential is qualitatively different from that for a metastable well because the periodic potential is multistable [53]. Thus, the particle having escaped a particular well may again be trapped due to the thermal fluctuations in another well. Moreover, jumps of either a single lattice spacing or of many lattice spacings are possible. Thus, the escape rate in a periodic potential is called the *jump* rate [50]. Moreover, we also saw that in order to estimate the quantum decay rate for all values of damping, Mel'nikov [8,9] extended the classical method of evaluation

of the escape rate Γ to account for quantum tunneling in a semiclassical way (see also Rips and Pollak [78]). By applying this approach to a cosine periodic potential, Georgievskii and Pollak [183] have obtained a universal expression for the quantum rate Γ above the crossover temperature between tunneling and thermal activation for the quantum Brownian dynamics in that potential.

Here, we solve the semiclassical master equation for the quantum Brownian dynamics in a periodic potential Eq. (471). In particular, we evaluate the dynamic structure factor. This factor allows one to evaluate various physical parameters [16,50]. Another of the most important characteristics associated with the Brownian motion in either a single-well or a multiwell potential is the friction and temperature dependence of the longest (overbarrier) relaxation time τ (or the inverse of the escape rate). The results of exact solutions yielded by the continued fraction method for the damping dependence of τ will be compared here with those of the Mel'nikov turnover equation for the quantum Kramers rate. Thus, the validity of the semiclassical approach may be ascertained.

We again use the semiclassical master equation [Eq. (448)] for the Wigner distribution function $W(x, p, t)$ [80,137,138,171,184]. Our present objective is to understand qualitatively how quantum effects treated in semiclassical fashion alter the classical Brownian motion in a periodic potential such as Eq. (471). Thus, now we shall apply matrix continued fractions to calculate various parameters and observables such as the dynamic structure function, the escape rate, and so on, directly from Eq. (448) and compare the results so obtained with available analytical solutions.

In order to represent the quantum master equation as a differential–recurrence relation for the statistical moments, we make the following rescaling in Eq. (448)

$$\begin{aligned} x' &= x/x_0, & p' &= p\eta/(mx_0), & t' &= t/\eta \\ U(x') &= -g \cos x', & \Lambda &= \hbar^2 / \left(48(\eta k_B T)^2 \right) \\ g &= V_0/(k_B T), & \beta' &= \eta\beta, & \eta &= \sqrt{mx_0^2/(2k_B T)} \end{aligned}$$

We then have

$$\begin{aligned} \frac{\partial W}{\partial t'} + p' \frac{\partial W}{\partial x'} - \frac{1}{2} \frac{\partial U}{\partial x'} \frac{\partial W}{\partial p'} + \frac{\Lambda}{4} \frac{\partial^3 U}{\partial x'^3} \frac{\partial^3 W}{\partial p'^3} \\ = \frac{\beta'}{2} \frac{\partial}{\partial p'} \left[2p'W + \left(1 + 2\Lambda \frac{\partial^2 U}{\partial x'^2} \right) \frac{\partial W}{\partial p'} \right] \end{aligned} \quad (472)$$

To investigate the process whereby the particle traverses the periodic potential Eq. (471), we must obtain the nonperiodic (running) solution of Eq. (472) [16]. Thus, we make the *Ansatz* [16]

$$W(x', p', t') = \int_{-1/2}^{1/2} w(k, x', p', t') e^{-ikx'} dk \quad (473)$$

where w is periodic in x' with period 2π and it is assumed that k is restricted to the first Brillouin zone, $-1/2 \leq k \leq 1/2$. The periodic function w can then be expanded in a Fourier series in x and in orthogonal Hermite functions $H_n(p')$ in p' [16,50], namely,

$$w(k, x', p', t') = \frac{e^{-p'^2 - U(x')/2}}{2\pi^{3/2}} \sum_{n=0}^{\infty} \sum_{q=-\infty}^{\infty} \frac{c_{n,q}(k, t')}{\sqrt{2^n n!}} H_n(p') e^{-iqx'} \quad (474)$$

By substituting Eq. (474) into Eq. (473), we see from Eq. (472) after some algebra that the Fourier coefficients $c_{n,q}(k, t')$ satisfy the 11-term differential–recurrence relation

$$\begin{aligned} \frac{d}{dt'} c_{n,q} + \beta' \left[n c_{n,q} - \Lambda g \sqrt{n(n-1)} (c_{n-2,q+1} + c_{n-2,q-1}) \right] \\ = i\sqrt{n/2} [(q+k)c_{n-1,q} + g(c_{n-1,q+1} - c_{n-1,q-1})/4] \\ + i\sqrt{(n+1)/2} [(q+k)c_{n+1,q} - g(c_{n+1,q+1} - c_{n+1,q-1})/4] \quad (475) \\ + i\Lambda g \sqrt{n(n-1)(n-2)/8} (c_{n-3,q+1} - c_{n-3,q-1}) \end{aligned}$$

By invoking the general method for solving matrix differential–recurrence equations [14,16,166,167], we have the solution of Eq. (475) for the spectra $\tilde{c}_{n,q}(k, \omega) = \int_0^{\infty} c_{n,q}(k, t) e^{-i\omega t} dt$ in terms of matrix continued fractions (details of this solution are given in Appendix B.5).

2. Calculation of Observables

Just as in the classical case, having determined $c_{n,q}(k, t)$, we can evaluate the dynamic structure factor $\tilde{S}(k, \omega)$ defined as

$$\tilde{S}(k, \omega) = \int_0^{\infty} S(k, t) e^{-i\omega t} dt \quad (476)$$

where $S(k, t) = \langle e^{ik[x(t) - x(0)]} \rangle_0$ is the characteristic function of the random variable $x(t) - x(0)$, that is, the displacement of the particle as it wanders through the

wells, and the angular brackets $\langle \rangle_0$ mean equilibrium ensemble averaging. The dynamic structure factor plays a major role in neutron and light scattering experiments [16]. Here, various physical parameters such as the escape rate, diffusion coefficient, and so on, can be evaluated from $\tilde{S}(k, \omega)$. The characteristic function $S(k, t')$ is calculated in a manner analogous to the classical case [16,50]

$$\begin{aligned}
S(k, t') &= \left\langle e^{ik[x'(t')-x'(0)]} \right\rangle_0 \\
&= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{ik(x'-x'_0)} W(x', p', x'_0, p'_0, t) dx' dx'_0 dp' dp'_0 \\
&= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{ik(x'-x'_0)} \int_{-1/2}^{1/2} e^{-ik_1(x'-x'_0)} w(k_1, x', p', x'_0, p'_0, t) \\
&\quad \times dk_1 dx' dx'_0 dp' dp'_0
\end{aligned}$$

(here $x'(0) = x'_0$, $x'(t) = x'$). The function $W(x', p', x'_0, p'_0, t) = \int_{-1/2}^{1/2} e^{-ik(x'-x'_0)} w(k, x', p', x'_0, p'_0, t) dk$ satisfies Eq. (472) with the initial condition

$$W(x', p', x'_0, p'_0, 0) = W_{\text{st}}(x'_0, p'_0) \quad (477)$$

where $W_{\text{st}}(x'_0, p'_0)$ is the equilibrium Wigner distribution function (which is a stationary solution of the master equation (448) [16,175]; see Appendix B). Noting that for a periodic function $f(x)$ and $-1/2 \leq k, k_1 \leq 1/2$ [16]

$$\int_{-\infty}^{\infty} e^{i(k-k_1)x} f(x) dx = \delta(k - k_1) \int_0^{2\pi} f(x) dx$$

and utilizing Eq. (474) and the orthogonality properties of the Hermite functions H_n , the characteristic function $S(k, t')$ becomes a series of the Fourier coefficients $c_{0,q}(k, t')$ as [16]

$$\begin{aligned}
S(k, t') &= \int_0^{2\pi} \int_0^{2\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} w(k, x', p', x'_0, p'_0, t) dx' dx'_0 dp' dp'_0 \\
&= \int_0^{2\pi} \int_{-\infty}^{\infty} w(k, x', p', t') dx' dp' = \sum_{q=-\infty}^{\infty} a_q c_{0,q}(k, t')
\end{aligned}$$

where

$$a_q = (2\pi)^{-1} \int_0^{2\pi} e^{-iqx - U(x')/2} dx'$$

and

$$w(k, x', p', t') = \int_0^{2\pi} \int_{-\infty}^{\infty} w(k, x', p', x'_0, p'_0, t) dx'_0 dp'_0$$

Thus, the dynamic structure factor $\tilde{S}(k, \omega)$ then becomes a series of the $\tilde{c}_{0,q}(k, \omega)$, namely,

$$\tilde{S}(k, \omega) = \sum_{q=-\infty}^{\infty} a_q \tilde{c}_{0,q}(k, \omega) \quad (478)$$

Thus having calculated $\tilde{S}(k, \omega)$, we may evaluate the escape (jump) rate Γ from Eq. (265) just as the classical case, namely,

$$\Gamma \approx 2 \int_0^{1/2} \tau^{-1}(k) dk \quad (479)$$

where

$$\tau(k) = \lim_{\omega \rightarrow 0} \frac{\tilde{S}(k, 0) - \tilde{S}(k, \omega)}{i\omega \tilde{S}(k, \omega)}$$

The escape (jump) rate Γ allows one to estimate using Eq. (479) the average longest relaxation time of the system since $\tau \sim \Gamma^{-1}$. Now $\tau^{-1}(k)$ can be expressed in terms of the jump rate Γ and the jump-length probabilities P_n (the probability of a jump of length $|n| x_0/2\pi$) as the trigonometric series [50]

$$\tau^{-1}(k) = \Gamma \sum_{n=1}^{\infty} P_n [1 - \cos(2\pi nk)] \quad (480)$$

with the result that the jump-length probabilities P_n may then be obtained in integral form as the Fourier coefficients of the Fourier expansion of $\tau^{-1}(k)$ as detailed in [50]

$$P_n = -2\Gamma^{-1} \int_0^{1/2} \tau^{-1}(k) \cos(2\pi nk) dk \quad (481)$$

Moreover, for high-potential barriers, in the jump diffusion limit, the jump-length probabilities P_n allow one to evaluate both the mean-square jump length $\langle l^2 \rangle$ and the diffusion coefficient D as [50]

$$\langle l^2 \rangle = 4\pi^2 x_0^2 \sum_{n=1}^{\infty} n^2 P_n \quad (482)$$

$$D \approx (\Gamma/2) \langle l^2 \rangle \quad (483)$$

The above equations describe in detail the diffusion process in the periodic potential.

3. Mel'nikov's Turnover Equation

As already mentioned, Mel'nikov [9] extended his solution of the classical Kramers turnover problem to include quantum effects in a semiclassical way. He did this initially by simply inserting the quantum mechanical transmission factor for a parabolic barrier into the classical integral equation for the energy distribution function yielded by the Wiener–Hopf method in the Kramers turnover region. In the approximation of Ohmic damping, he derived a universal formula for the quantum rate Γ_M [see Eq. (463)] valid for all values of damping above the crossover temperature between tunneling and thermal activation

$$\Gamma_M = \Gamma^{\text{IHD}} \Upsilon \quad (484)$$

Later as we saw in detail in Section III.A, he improved upon this initial result following Larkin and Ovchinnikov [11] by generalizing it to a system coupled to a bath with Johnson–Nyquist quantum thermal noise spectrum. Now Mel'nikov and Sütö [185] have applied the latter development to quantum Brownian motion in a tilted cosine potential [the zero tilt case corresponds to Eq. (471)]. Furthermore, Rips and Pollak [78] gave a consistent solution of the quantum Kramers turnover problem demonstrating how the Mel'nikov equation (484) can be obtained without his *ad hoc* interpolation between the weak and strong damping regimes. Finally, Georgievskii and Pollak [183] treated the escape rate problem in a periodic cosine potential showing that the quantum depopulation factor Υ in Eq. (484) is

$$\Upsilon = 4 \int_0^1 \sin^2(\pi k) F(k) dk \quad (485)$$

The function $F(k)$ is (in our notation)

$$F(k) = \exp \left\{ \frac{a \sin a}{\pi} \int_{-\infty}^{\infty} \ln \left[\frac{1 - e^{-2R(x)}}{1 + e^{-2R(x)} - 2e^{-R(x)} \cos(2\pi k)} \right] \frac{dx}{\cosh(2ax) - \cos a} \right\} \quad (486)$$

where

$$R(x) = \frac{\pi\beta'}{\sqrt{3\Lambda}} \int_{-\infty}^{\infty} \frac{\cosh(\sqrt{\Lambda}y) - \cos(2\sqrt{\Lambda}xy)}{y \sinh(\sqrt{\Lambda}y) \cosh^2[\pi y/(2\sqrt{6g})]} dy \quad (487)$$

and $a = \sqrt{3\Lambda} \left(\sqrt{\beta'^2 + 2g} - \beta' \right)$. If absolute precision is unnecessary, the function $R(x)$ from Eq. (487) can be replaced by its classical limit $R(x) \approx \Delta(x^2 + 1/4)$, where $\Delta = 8\beta' \sqrt{2g}$. We may now estimate using the Wigner function method the quantum escape rate Γ^{IHD} [and thus Γ_{M} via Eq. (484)] by adapting results of the classical Kramers escape rate theory [15] (see Appendix D). The quantum escape rate Γ^{IHD} is then

$$\Gamma^{\text{IHD}} = \frac{\Xi}{2\pi\eta} \left(\sqrt{\beta'^2 + 2g} - \beta' \right) e^{-2g} \quad (488)$$

where the quantum correction factor is given by Eq. (13), namely,

$$\Xi = \frac{\omega_C \sinh [\hbar\omega_A/(2kT)]}{\omega_A \sin [\hbar\omega_C/(2kT)]} = 1 + 2g\Lambda + \dots \quad (489)$$

is or (in full agreement with quantum TST [22]), $\omega_C = \sqrt{|V''(x_C)|/m} = \omega_A = \sqrt{V''(x_A)/m}$. The form of Eq. (488) appears to be consistent with our (Section III.B) conception of a quantum Brownian particle as being embedded in a classical bath with the quantum effects in the bath–particle interaction arising via the dependence of the diffusion coefficient on the derivatives of the potential in the quantum master equation. The simple result follows from the exact solution for the Wigner equilibrium distribution function for the harmonic oscillator given in Refs [157,158].

In the context of the determination of the IHD quantum Kramers rate, we remark that the analysis of Wolynes [150] as well as that of Pollak [18] (which we have explained in detail) involve quantization of *both* bath and particle just as do methods [7] based on Langer’s analytical continuation of the free energy.

Moreover, we showed that the quantum mechanical enhancement factor Ξ yielded by all these calculations is for Ohmic friction [22,150]

$$\Xi_W = \prod_{n=1}^{\infty} \frac{(\hbar\omega_A)^2 + (2\pi n k_B T)^2 + 2\pi n \hbar \beta k_B T}{-(\hbar\omega_C)^2 + (2\pi n k_B T)^2 + 2\pi n \hbar \beta k_B T} \quad (490)$$

If the condition $\hbar\beta/(k_B T) \ll 2\pi$ is fulfilled, we have the TST result as $\lim_{\hbar\gamma/(kT) \rightarrow 0} \Xi_W = \Xi$ [22]. Thus recovering the result embodied in Eq. (488). The *damping independent* Ξ is then a fair approximation to Ξ_W suggesting that replacement of the equilibrium distribution function by that of the closed system may ultimately yield reasonable semiclassical approximations to the actual time dependent quantum distribution. A comprehensive analysis of Eq. (490) has been made by Hänggi et al. [186] and also by Weiss [22]. They show how the product involving the Matsubara frequencies in Eq. (490) may be written as gamma functions consequently Wigner's original quantum correction [24] is recovered when $T \gg (\beta/\omega_C)^2 T_c$.

Finally the jump-length probabilities can be estimated as [50]

$$P_n^M = - \frac{\int_0^{1/2} \sin^2(\pi k) F(k) \cos(2\pi n k) dk}{\int_0^{1/2} \sin^2(\pi k) F(k) dk} \quad (491)$$

where $F(k)$ is defined by Eq. (486) and the superscript M denotes analytical calculation (as in Ref. [50]).

The results yielded by the analytical theory may now be compared with the matrix continued fraction solution.

4. Comparison of Exact Matrix Solution with Approximate Analytical Formula

The real and imaginary parts of the normalized dynamic structure factor $\tilde{S}(k, \omega)/\tilde{S}(k, 0)$ are shown in Fig. 29 for various barrier heights g with the damping parameter $\beta' = 10$, and wave number $k = 0.2$. For comparison, we also show in this figure the pure Lorentzian spectra

$$\frac{\tilde{S}(k, \omega)}{\tilde{S}(k, 0)} = \frac{1}{1 + i\omega\tau_k} \quad (492)$$

where the relaxation time $\tau_k = \tau_M(k)$ is related to the escape Γ^M from Eq. (484) via $\Gamma^M = 2 \int_0^{1/2} \tau_M^{-1}(k) dk$. Apparently the simple Eq. (492) perfectly describes the low-frequency part of the normalized dynamic structure factor $\tilde{S}(k, \omega)/\tilde{S}(k, 0)$.

The longest relaxation time $\tau = \Gamma^{-1}$ predicted by the turnover formula, Eq. (484), and the inverse decay rate calculated numerically by matrix continued fractions are shown in Fig. 30 as functions of the damping parameter γ' for

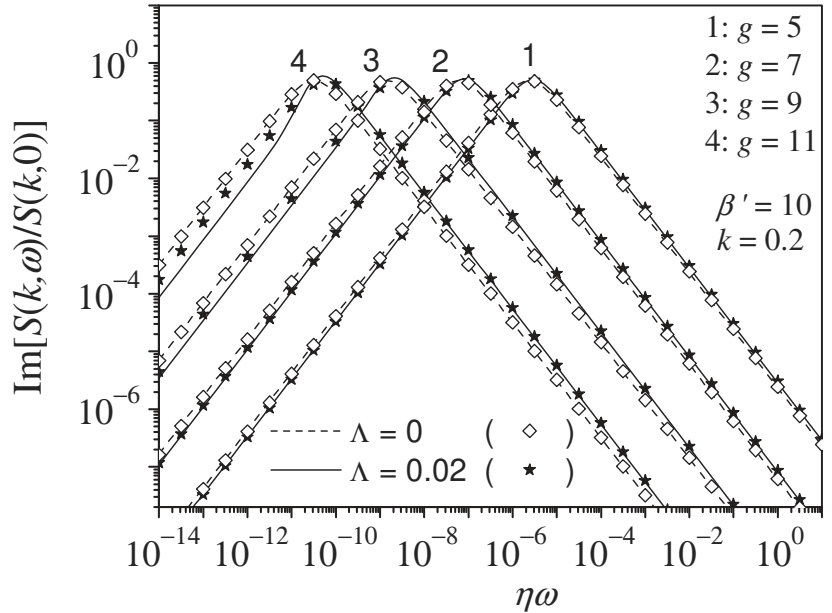
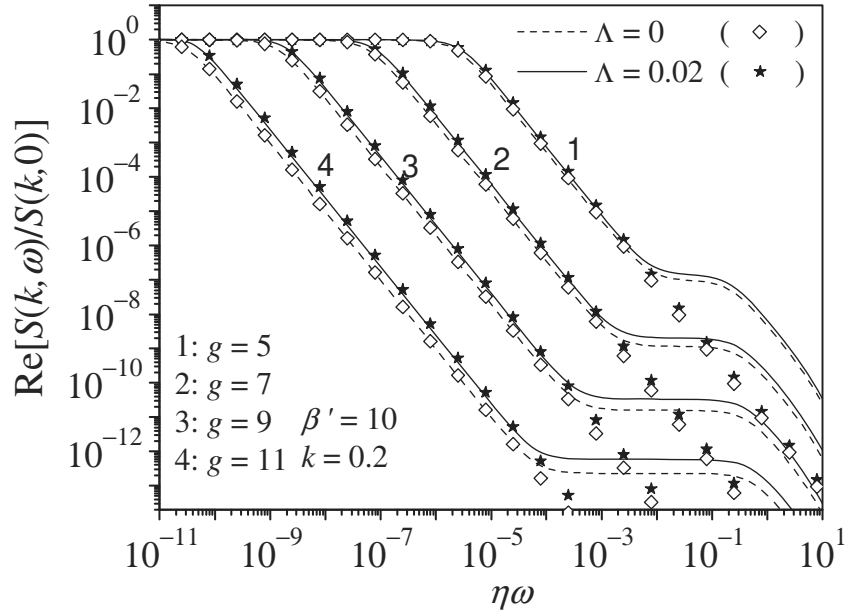


Figure 29. The real and imaginary parts of the normalized dynamic structure factor $\tilde{S}(k, \omega)/\tilde{S}(k, 0)$ versus $\omega\eta$ for various values of barrier parameter $g = 5, 7, 9,$ and 11 ; the damping coefficient $\beta' = 10$ and $k = 0.2$. Solid and dashed lines: the matrix continued fraction solution with $\Lambda = 0.02$ and $\Lambda = 0$ (classical case), respectively. Stars and open diamonds: Eq. (492) with $\Lambda = 0.02$ and $\Lambda = 0$, respectively.

various values of the quantum parameter Λ (the curves and open circles corresponding to $\Lambda = 0$ are the classical results). The IHD [Eq. (488)], asymptotes for τ are also shown for comparison. Using the Wigner stationary distribution W_{st} and imposing the condition $\hat{M}_{\text{D}}W_{\text{st}} = 0$ gives the correct dependence of the escape rate (τ decreases with increasing Λ). If the condition $\widehat{M}_{\text{D}}W_{\text{st}} = 0$ is not fulfilled (e.g., the diffusion coefficient D_{pp} is regarded as a constant), *the behavior of the decay rate is not reproduced at all* (see Fig. 30). The quantitative agreement in damping behavior may be explained as follows. As we saw for many other systems the escape rate as a function of the barrier height parameter g for large g is approximately Arrhenius-like and arises from an *equilibrium* property of the system (namely the stationary distribution at the bottom of the well). On the other hand, the damping dependence of the escape rate is due to *nonequilibrium* (dynamical)

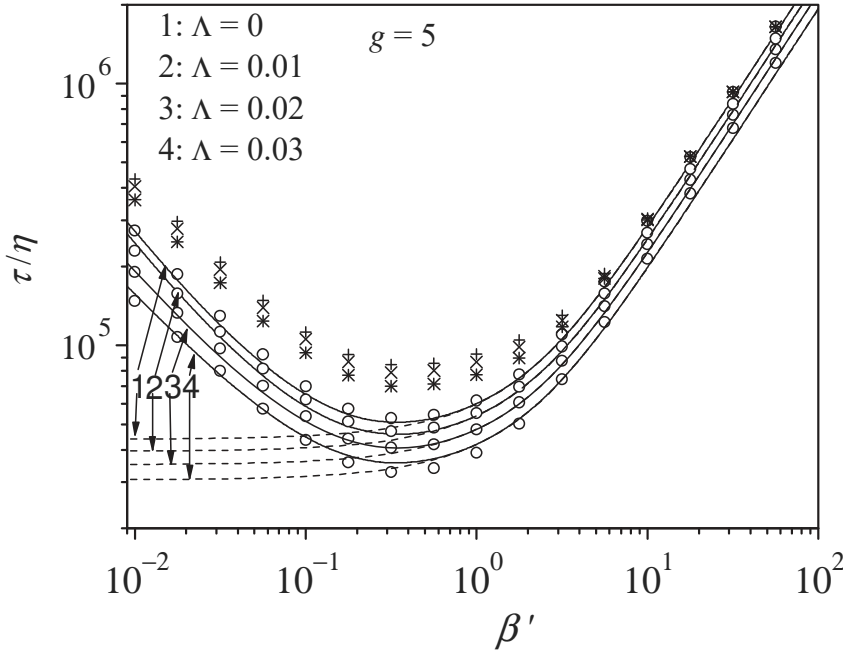


Figure 30. The normalized longest relaxation time τ/η versus β' for the barrier parameter $g=5$ and various values of the quantum parameter $\Lambda=0$ (classical case), 0.01, 0.02, and 0.03. Solid lines: Eq. (484). Dashed lines: the IHD Eq. (488). Open circles: the matrix continued fraction solution of the master equation (472). Symbols: the matrix continued fraction solution of Eq. (472) with the constant diffusion coefficient $D_{pp} = \beta m k_B T$.

properties of the system so that the Mel'nikov approach [8,9] should yield the relaxation time for all values of the damping. The longest relaxation time τ predicted by the Mel'nikov turnover equation (484) and the inverse decay rate calculated numerically via matrix continued fractions are shown in Fig. 31 as functions of β' for various barrier heights. The IHD [Eq. (488)] asymptotes for τ are also shown for comparison. The higher the barrier parameter g the more pronounced is the quantum correction.

The results of calculations of the jump-length probabilities P_n and P_n^M from Eqs. (481) and (491) are shown in Fig. 32 for $\Lambda = 0$ (classical case) and $\Lambda = 0.02$. The numerical results are consistent with an asymptotic exponential decay of the P_n^M . However, for large n and small friction parameter β' , deviations from the exponential behavior may appear [50].

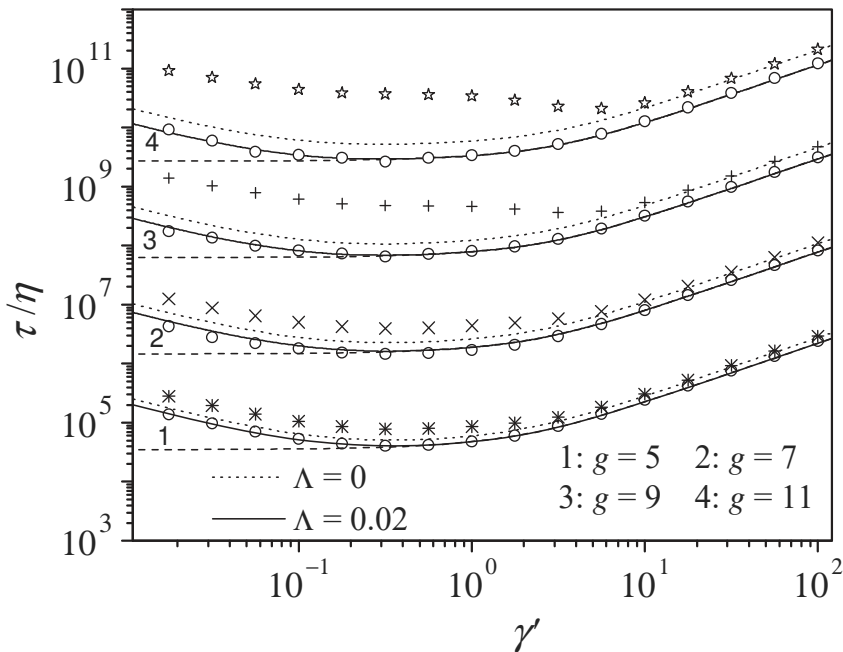
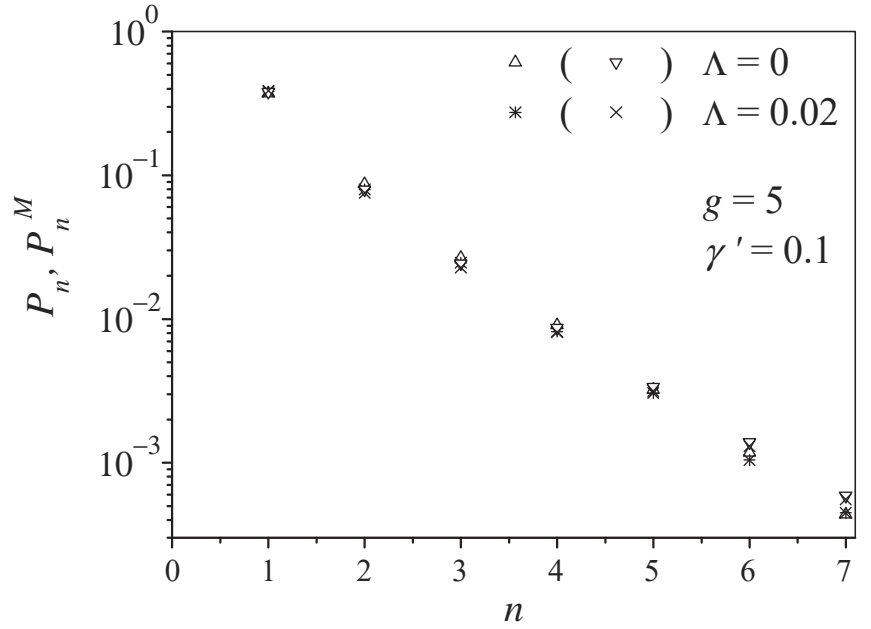


Figure 31. τ/η versus β' for various values of the barrier parameter $g=5, 7, 9,$ and 11 . Solid and dotted lines: Eq. (484) for $\Lambda=0.02$ and $\Lambda=0$ (classical case), respectively. Dashed lines: the IHD Eq. (488) for $\Lambda=0.02$. Open circles: the matrix continued fraction solution of Eq. (472). Symbols: the matrix continued fraction solution of Eq. (472) with the constant diffusion coefficient $D_{pp} = \beta m k_B T$.

Figure 32. The jump-length probabilities P_n and P_n^M for the barrier parameter $g=5$, damping parameter $\beta'=0.1$, and two values of the quantum parameter $\Lambda=0$ (up and down triangles; classical case) and $\Lambda=0.02$ (stars and crosses). Up triangles and stars: Eq. (481); down triangles and crosses: Eq. (491).



In spite of the very good agreement between the numerical results and the turnover equation (484) for $\Lambda < 0.03$, a difference between numerical and analytical results exists in the IHD region for larger values of Λ . The disagreement indicates that in order to improve the accuracy for these values of Λ , additional terms of the order of Λ^2 , and on, should be included in the master equation. These higher order quantum correction terms to the master Eq. (448), may be calculated, in principle, to any desired degree r of \hbar^{2r} . However, with increasing r , the correction terms become more complicated. In particular, the explicit form of the master equation (448) containing the terms up to $o(\hbar^4)$ is

$$\begin{aligned} & \frac{\partial W}{\partial t} + \frac{p}{m} \frac{\partial W}{\partial x} - \frac{\partial V}{\partial x} \frac{\partial W}{\partial p} + \frac{\hbar^2}{24} \frac{\partial^3 V}{\partial x^3} \frac{\partial^3 W}{\partial p^3} - \frac{\hbar^4}{1920} \frac{\partial^5 V}{\partial x^5} \frac{\partial^5 W}{\partial p^5} + \dots \\ & = \beta \frac{\partial}{\partial p} \left[pW + mk_B T \left\{ 1 + \frac{[\hbar/(k_B T)]^2}{12m} V'' - \frac{[\hbar/(k_B T)]^4}{1440m^2} \right. \right. \\ & \quad \left. \left. \times \left[6V''' V' + 2V''^2 + 3V^{(4)} \left(\frac{p^2}{m} - 5k_B T \right) \right] \right\} \frac{\partial W}{\partial p} \right] + \dots \end{aligned}$$

We emphasize that we use the equilibrium Wigner function $W_{st}(x, p)$ for vanishing damping ($\beta \rightarrow 0$). In quantum systems, however, the equilibrium distribution $W_\beta(x, p)$ is damping dependent [22]. The damping dependence of $W_\beta(x, p)$ is unknown for arbitrary $V(x)$. However, $W_\beta(x, p)$ always reduces to $W_{st}(x, p)$ in the high-temperature limit. Moreover, the difference between $W_\beta(x, p)$ and $W_{st}(x, p)$ may be negligible in a large range of variation of the model parameters. Thus, one would expect that the evolution equation (448) is a reasonable approximation for the kinetics of a quantum Brownian particle in a potential $V(x)$ when $\hbar\beta/(k_B T) \leq 1$.

The justification of the master equation (448) for the quantum Brownian motion of a particle in a periodic (cosine) potential (by showing that the solution of that equation for the longest relaxation time is in agreement with that predicted by quantum rate theory) and the successful extension to the quantum case of the matrix continued fraction methods associated with the classical Fokker–Planck equation are our main results. In particular, the dependence of the diffusion coefficient on the derivatives of the potential (with consequent lowering of the potential barrier) arising from the *Ansatz* of a Wigner stationary distribution for the equilibrium solution of the open system successfully reproduces escape rates predicted by the quantum generalization of the Kramers escape rate theory and its various extensions to the turnover region as applied to the cosine potential. Furthermore, the successful extension of the classical matrix continued fraction method [14,16] to the semiclassical quantum master equation allows one to accurately calculate in semiclassical fashion, quantum corrections to the appropriate dynamical quantities such as correlation functions and susceptibilities (cf. the calculation of the dynamic structure factor). This is in general impossible using quantum reaction rate theory since that theory as presently formulated does not involve an explicit master equation. We further remark that the agreement obtained between escape rates calculated from quantum reaction rate theory in the manner of Georgievskii and Pollak [183] and those from the master equation (448) (cf. Figs. 30 and 31) also constitutes a verification of quantum rate theory for the potential in question. We reiterate that the dependence of the diffusion coefficient on the derivatives of the potential arising from the imposition of the Wigner stationary distribution is crucial. If this dependence is not taken into account, for example, considering the diffusion coefficient as constant, the characteristic lowering of the barrier produced by the quantum tunneling near the top of the barrier cannot be reproduced neither can one regain the results of quantum reaction rate theory.

Our calculations that have been outlined for mechanical systems with separable and additive Hamiltonians may possibly be extended to particular (nonseparable) spin systems such as a single-domain ferromagnetic particle since the giant spin Hamiltonian of the particle may be mapped onto an equivalent single mechanical particle Hamiltonian. This transformation is of particular importance concerning the existence of macroscopic quantum tunneling phenomena in such ferromagnetic particles and also in the discussion of the crossover region between reversal of magnetization by thermal agitation and reversal by macroscopic quantum tunneling that is of current topical interest [26].

IV. CONCLUSION

In this chapter, we have attempted to summarize, with the needs of the graduate student in mind and in accordance with the stated aims of the *advances*, the

main features of the calculation of the Kramers escape rate for all values of the damping in both the classical and the semiclassical cases. The inverse escape rate of course yields the lifetime of a particle in a potential well. By way of a check on the veracity of our analytical calculations, we have also compared the analytical escape rates with those numerically determined in the classical case from the appropriate Fokker–Planck equation and in the quantum case from the appropriate semiclassical master equation. The latter equation is derived by extending Wigner’s phase space formulation of quantum mechanics of closed systems to the open system pertaining to quantum Brownian particles, by postulating (as in the classical Brownian motion) a truncated Kramers–Moyal expansion for the collision integral. This accounts for the bath–particle dissipation in the single-particle distribution function. However, a marked difference from the classical case is that in the semiclassical equation for the evolution of the single-particle or reduced Wigner function in phase space the diffusion coefficients are in general functions of the derivatives of the potential. The master equation is solved in the manner of Wigner [139] by means of a high-temperature perturbation expansion in Planck’s constant. This procedure then yields a hierarchy of perturbed equations with the zero order of perturbation being the classical Fokker–Planck equation. The first order of perturbation equation stems from the classical Fokker–Planck operator (which represents the transition matrix) forced by quantum terms involving the zero-order solution and so on in the usual manner of perturbation theory. This prescription then allows one to apply all the quasianalytical numerical methods, notably the matrix continued fractions developed for the Fokker–Planck equation, to the quantum master equation. Thus, all characteristic times, escape rates, and susceptibilities may be calculated just as the corresponding classical quantities. In general, the escape rates or lifetimes numerically calculated from either the Fokker–Planck or the master equation as the case may be, are in good agreement with the classical and semiclassical Kramers rates.

Regarding the analytical expressions for the escape rates based on the Kramers theory taking first the classical case and considering for simplicity an isolated well, the vital concept in the underdamped case is the undamped librational motion of a particle in the well with energy equal to the barrier energy. The noisy motion due to dissipation and fluctuations arising from the bath then causes the deterministic librational motion couched in terms of the closed librational trajectory and governed by Newtonian dynamics to become stochastic, that is, the trajectories diffuse in energy space as a function of action (a notion originally due to Kramers). Thus, a thermal fluctuation may cause a hitherto closed trajectory to become open, which then constitutes a separatrix traveling on which a particle exits the well. The first step in the calculation of the escape rate in the classical underdamped case is then the determination of the Green function or transition probability that governs the diffusion of energy of a particle due to thermal agitation in one cycle of the librational motion in the well. The population or energy distribution of the

escaping particles may then be written down by the principle of superposition as the solution of an integral equation of the Wiener–Hopf type. This equation may be solved subject to appropriate boundary conditions as we have exhaustively described, yielding the classical escape rate in the entire underdamped region (lying between zero damping and intermediate damping corresponding to TST) in terms of a depopulation factor. That factor describes the depopulation of the upper regions of the well due to escape (i.e., a loss of particles causing a disturbance to the Maxwell–Boltzmann distribution in the well) over the barrier. Moreover, the depopulation factor is universal in the sense that it retains the same integral form for all well-behaved potentials. Furthermore, the only parameter is that introduced initially by Kramers in his discussion of the very low damping rate, namely, Δ , the ratio of the energy loss per cycle of a particle librating in the well with energy equal to the barrier energy to the thermal energy. A formula for the escape rate valid for all values of the dissipation to the bath is then written down using Mel’nikov’s [8–10] *ad hoc* assumption that the prefactor of this rate is simply the underdamped prefactor multiplied by the Kramers IHD prefactor. We have extensively reviewed the criticism of this assumption by Pollak et al. [12] based on treating the Brownian particle as an entity bilinearly coupled to a string that plays the role of friction with the motion of the particle being determined by a generalized Langevin equation.

Turning now to the quantum case where we confine ourselves to relatively high temperatures as detailed in the text, we first treat the IHD quantum rate by recognizing that the multidimensional Kramers rate is simply the TST rate in the complete phase space of the particle plus bath system as described by Langer [13], Grote and Hynes [2], Pollak [12,18], and so on. Thus given an appropriate model for the bath–particle coupling and a suitable generalized Langevin equation, one may simply calculate the IHD rate from harmonic quantum TST. This calculation is accomplished using Pollak’s model of a particle governed by a generalized Langevin equation and bilinearly coupled to a bath of harmonic oscillators. In doing this, we have eschewed the path integral methods of Wolynes [150] and Mel’nikov [8] as in general the calculations involving these are less transparent than those of Pollak [18].

In the underdamped quantum case our primary objective as before is to calculate the Green function that now describes as well as the thermal diffusion of energy in one cycle of the librational motion, the change in energy per cycle due to high-temperature tunneling in the separatrix region infinitesimally close to the top of the barrier. Now in the classical case, we calculated the Green function by transforming the Fokker–Planck equation into (slow) energy–(fast) position variables ultimately leading to an energy–action diffusion equation that is valid in the vicinity of the barrier where it describes the nonequilibrium events occurring there. This equation may be solved using Fourier transforms to yield the probability distribution of the change in energy per cycle due to thermal fluctuations given a sharp distribution of energy at the beginning of the cycle. The Green function represents a relatively

sharply peaked Gaussian distribution with variance given by the Kramers loss parameter, namely, the energy loss per cycle divided by the thermal energy. The distribution is sharply peaked because the diffusion of energy in one cycle is very small by hypothesis.

In the quantum case, however, no such procedure is available to us as we can no longer use the Fokker–Planck equation. Rather the Green function that still forms the kernel of the integral equation for the population of escaping particles must be represented by the statistical density matrix that now includes both thermal and quantum tunneling effects describing the (quantized) change of energy in one cycle near the barrier top. Mindful of the semiclassical nature of our treatment we may then use the JWKB method whereby the energy levels in the vicinity of the barrier, of a librational trajectory with energy equal to the barrier energy may be regarded as quasicontinuous. This procedure allows one to calculate in the interaction representation in the first order of perturbation theory the quantum transition probability via (Fermi’s Golden Rule) associated with the position operator in the presence of the Boson bath, that is, Eq. (403). The JWKB approximation in effect permits one to calculate the matrix elements associated with the position operator in terms of the Fourier transform over time of the classical librational trajectory. The quantum transition probability per cycle of transition from energy state j to energy state f is then effectively the output spectral density if the Johnson–Nyquist noise is regarded as being passed through a filter with the transfer function given by the Fourier transform over time of the classical trajectories, that is, the matrix elements of the position operator. This is essentially the first step in the calculation of the quantum Green function. The next step is to again make use of the matrix elements of the position operator in terms of the Fourier transform of the classical trajectory. This step ultimately allows one starting from the Hamiltonian of the particle as perturbed by the noise to formally write via the Schrödinger equation in the interaction picture the probability amplitude of the evolution operator $\hat{\Phi}$ for the state vector of the noise-induced energy transitions in a cycle of the motion in the form of a (quasicontinuous) Fourier transform pair after an involved calculation as detailed in the text. Next by taking a thermal average in the presence of the noise and using the Gaussian properties of the noise, one may prove that the statistical density matrix that is the Green function is the inverse Fourier transform over an exponential characteristic function in the λ domain. This characteristic function is entirely analogous to that of the Gaussian distribution of the classical case. However, unlike the latter where the argument of the exponent in the characteristic function in the λ domain, namely, $\Delta(\lambda^2 + 1/4)$, is always known explicitly, the argument in the quantum case must be calculated by taking the Fourier transform in the λ domain of the (Golden Rule) quantum transition probability equation (403). Hence, the expression for the quantum Green function leads to much more complicated calculations than in the classical one as the matrix elements, and so on, must be explicitly determined in any particular case. Thus,

supposing that the potential in the vicinity of the barrier may be represented by an inverted parabola, then dividing the Green function by the reflection coefficient for the parabolic barrier and finally using the principle of superposition we have the integral equation for the population of escaping particles. Once more this is an equation of the Wiener–Hopf type and may be solved to yield the escape rate in the entire underdamped region at temperatures above the critical temperature at which the parabolic approximation to the barrier potential fails. We emphasize that unlike the classical case where the dynamical prefactor is a function only of the Kramers dissipation parameter Δ the prefactor is now also a function of the quantum parameter $\hbar\omega_C/(2\pi k_B T)$, where ω_C is the frequency associated with the barrier. The escape rate in the entire range of damping is then determined using the same *ad hoc* assumption as before namely the quantum rate is determined by the product of the IHD and underdamped rates. This assumption has been examined in detail by Rips and Pollak again using the model of a particle coupled bilinearly to a harmonic oscillator bath. Recalling the beginning of these conclusions, the quantum escape rate calculated analytically by the procedures we have outlined exhibits good agreement in general with the Wigner phase space master equation.

This concludes our long discussion of the classical and quantum treatment of the Kramers turnover problem and its application to the calculation of the lifetime of a particle in a potential well that we hope will serve as an introduction to the subject for the beginner.

ACKNOWLEDGMENT

The work described in this chapter forms part of the EU COST action MP1006 Fundamental Principles in Quantum Physics.

APPENDIX A: WIENER–HOPF METHOD

Following [8–10], we can solve the integral equations (149) and (151) by the Wiener–Hopf method by introducing the Fourier transforms [8,30]

$$\varphi_i^\pm(\lambda) = \tau_{\text{TST}}(\phi_i) \int_{-\infty}^{\infty} f_i(E) U(\pm E) e^{-(i\lambda+1/2)E/(k_B T)} dE \quad (\text{A1})$$

where

$$\tau_{\text{TST}}^{-1}(\phi_i) = \frac{\sqrt{V''(\phi_i)/I}}{2\pi} e^{V(\phi_i)/(k_B T)} \quad (\text{A2})$$

and $\phi_i = \phi_{\min_i}$ are the potential minima in the i th well (recalling that $V(\phi_i)$ is negative, see Fig. 4). The prefactor $\tau_{\text{TST}}(\phi_i)$ of the Fourier transformation that is introduced for notational convenience is suggested by Eq. (19). Applying this transformation to the integral equations (149) and (151), we have

$$\varphi_1^+(\lambda) + \varphi_1^-(\lambda) = [1 - G_1(\lambda)][\varphi_1^-(\lambda) + \varphi_2^+(\lambda)] \quad (\text{A3})$$

$$\varphi_2^+(\lambda) + \varphi_2^-(\lambda) = [1 - G_2(\lambda)][\varphi_2^-(\lambda) + \varphi_1^+(\lambda)] \quad (\text{A4})$$

where $G_i(\lambda)$ is related to the Fourier transform of the Green function $\tilde{g}_i(\lambda)$ via

$$G_i(\lambda) = 1 - \tilde{g}_i(\lambda) = e^{-\Delta_i(\lambda^2+1/4)} \quad (\text{A5})$$

and $\Delta_i = \beta S_i / (k_B T)$. Now, Eq. (154) in turn can be represented as

$$\tau^{-1} = \frac{2A(\Delta_1, \Delta_2)}{\sqrt{|V''(0)|/I}} \left[\sqrt{\frac{\beta^2}{4} + |V''(0)|/I} - \frac{\beta}{2} \right] \left[\tau_{\text{TST}}^{-1}(\phi_1) + \tau_{\text{TST}}^{-1}(\phi_2) \right] \quad (\text{A6})$$

where

$$A(\Delta_1, \Delta_2) = \varphi_1^+(i/2) - \varphi_2^+(i/2) = \varphi^+(i/2) \quad (\text{A7})$$

Here, we have introduced the function $\varphi(\lambda) = \varphi_1(\lambda) - \varphi_2(\lambda)$. An equation for $\varphi(\lambda)$ can be obtained by subtracting Eq. (A4) from Eq. (A3). We have

$$\varphi^+(\lambda) + \frac{G_1(\lambda)G_2(\lambda)}{G_{12}(\lambda)}\varphi^-(\lambda) = 0 \quad (\text{A8})$$

where

$$G_{12}(\lambda) = G_1(\lambda) + G_2(\lambda) - G_1(\lambda)G_2(\lambda) = 1 - e^{-(\Delta_1+\Delta_2)(\lambda^2+1/4)} \quad (\text{A9})$$

Equation (A8) is now in a form where one may apply the Wiener–Hopf method. In order to use it we rewrite Eq. (A8) as

$$\ln[-\varphi^+(\lambda)] = \ln G_1(\lambda) + \ln G_2(\lambda) - \ln G_{12}(\lambda) + \ln \varphi^-(\lambda) \quad (\text{A10})$$

The function $G_i(\lambda)$ may now be decomposed as

$$G_i(\lambda) = G_i^+(\lambda)G_i^-(\lambda) \quad (\text{A11})$$

where by Cauchy's theorem

$$G_i^\pm(\lambda) = \exp \left[\pm \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{\ln G_i(\lambda')}{\lambda' - \lambda \mp i0} d\lambda' \right] \quad (\text{A12})$$

Equation (A10), thus, has the form

$$\begin{aligned} & \ln[-\varphi^+(\lambda)] - \ln G_1^+(\lambda) - \ln G_2^+(\lambda) + \ln G_{12}^+(\lambda) \\ & = \ln G_1^-(\lambda) + \ln G_2^-(\lambda) - \ln G_{12}^-(\lambda) + \ln \varphi^-(\lambda) \end{aligned} \quad (\text{A13})$$

The functions f_1 and f_2 must satisfy the boundary conditions that deep in the wells they both become Maxwell–Boltzmann distributions so that

$$f_i(E) \sim \frac{\sqrt{V''(\phi_i)/I}}{2\pi k_B T} e^{-[E-V(\phi_i)]/(k_B T)}, \quad -E \gg k_B T \quad (\text{A14})$$

As a consequence, the functions $\varphi_i^\pm(\lambda)$ from Eq. (A1) have poles (the choice of the prefactor in that equation should now be evident)

$$\varphi_i^\pm(\lambda) = \frac{-i}{\lambda \pm i/2}, \quad |\lambda + i/2| \ll 1 \quad (\text{A15})$$

As the functions on the left-hand and on the right-hand side of Eq. (A13) are analytical in different half-planes for complex λ they should equal an entire function, which satisfies Eq. (A15) [8]

$$\varphi^+(\lambda) = i \frac{G_1^-(-i/2)G_2^-(-i/2)G_1^+(\lambda)G_2^+(\lambda)}{(\lambda + i/2)G_{12}^+(-i/2)G_{12}^-(\lambda)} \quad (\text{A16})$$

Hence in Eq. (A6)

$$A(\Delta_1, \Delta_2) = \frac{A(\Delta_1)A(\Delta_2)}{A(\Delta_1 + \Delta_2)} \quad (\text{A17})$$

where

$$A(S_i) = |G_i^+(i/2)|^2 \quad (\text{A18})$$

Substituting G_i^+ from Eq. (A12) into Eq. (A18) and noting Eqs. (148) and (156), one obtains the depopulation factor $A(\Delta)$ in Eq. (119) bridging the VLD and TST results.

APPENDIX B: MATRICES AND VECTORS INVOLVED IN THE MATRIX CONTINUED FRACTION SOLUTIONS

B.1. Fixed Axis Rotator in a Symmetrical Double-Well Potential

The column vector $\mathbf{C}_1(0)$ and the matrix elements of the infinite square matrices \mathbf{Q}_n^- ($n > 2$) and \mathbf{Q}_n^+ ($n > 1$) are

$$\mathbf{C}_1(0) = \frac{i}{2I_0(\sigma)} \begin{pmatrix} \vdots \\ I_2(\sigma) + I_3(\sigma) \\ 0 \\ -I_2(\sigma) - I_1(\sigma) \\ 0 \\ I_0(\sigma) + I_1(\sigma) \\ -I_0(\sigma) - I_1(\sigma) \\ 0 \\ I_2(\sigma) + I_1(\sigma) \\ 0 \\ -I_2(\sigma) - I_3(\sigma) \\ \vdots \end{pmatrix} \quad (\text{B1})$$

$$(\mathbf{Q}_n^+)_{p,q} = -(i/2)p\delta_{pq} \quad (\text{B2})$$

$$(\mathbf{Q}_n^-)_{p,q} = -i(n-1)(\delta_{pq+2\sigma} + p\delta_{pq} - \delta_{pq-2\sigma}) \quad (\text{B3})$$

where $-\infty < p, q < +\infty$. The matrices \mathbf{Q}_2^- and \mathbf{Q}_1^+ are again obtained by omitting the column corresponding to $q = 0$ from \mathbf{Q}_n^- for $n = 2$ and by omitting the row corresponding to $p = 0$ from \mathbf{Q}_n^+ for $n = 1$, respectively.

B.2. Fixed Axis Rotator in an Asymmetrical Double-Well Potential

The column vector $\mathbf{C}_1(0)$ and the matrix elements of the infinite square matrices \mathbf{Q}_n^- ($n > 2$) and \mathbf{Q}_n^+ ($n > 1$) are

$$\mathbf{C}_1(0) = \begin{pmatrix} \vdots \\ c_{0,-2}(0) \\ c_{0,-1}(0) \\ c_{0,1}(0) \\ c_{0,2}(0) \\ \vdots \end{pmatrix}$$

$$(\mathbf{Q}_n^+)_{pq} = -\frac{i}{2} p \delta_{pq}$$

$$(\mathbf{Q}_n^-)_{p,q} = -i(n-1) (\delta_{pq-2\sigma} + \delta_{pq-1} 2h\sigma + p\delta_{pq} - \delta_{pq+1} 2h\sigma - \delta_{pq+2\sigma})$$

where $-\infty < p, q < +\infty$. The matrices \mathbf{Q}_2^- and \mathbf{Q}_1^+ are not square and are again obtained by omitting the column corresponding to $q = 0$ from \mathbf{Q}_n^- for $n = 2$ and by omitting the row corresponding to $p = 0$ from \mathbf{Q}_n^+ for $n = 1$, respectively.

The initial conditions $c_{0,q}(0)$

$$\begin{aligned} c_{0,q}(0) &= \langle e^{-iq\phi} \cos \phi \rangle_0 - \langle \cos \phi \rangle_0 \langle e^{-iq\phi} \rangle_0 \\ &= \int_0^{2\pi} \cos \phi e^{-iq\phi} W_0(\phi) d\phi - \int_0^{2\pi} \cos \phi W_0(\phi) d\phi \int_0^{2\pi} e^{-iq\phi} W_0(\phi) d\phi \end{aligned}$$

where $W_0(\phi)$ is the equilibrium distribution in configuration space defined by Eq. (203), can be evaluated analytically in terms of the modified Bessel functions of the first kind I_n [72] because

$$\begin{aligned} \langle e^{-iq\phi} \cos \phi \rangle_0 &= \frac{\sum_{m=-\infty}^{\infty} I_m(\sigma) [I_{-2m+q+1}(4\sigma h) + I_{-2m+q-1}(4\sigma h)]}{2 \sum_{m=-\infty}^{\infty} I_m(\sigma) I_{-2m}(4\sigma h)} \\ \langle e^{-iq\phi} \rangle_0 &= \frac{\sum_{m=-\infty}^{\infty} I_m(\sigma) I_{-2m+q}(4\sigma h)}{\sum_{m=-\infty}^{\infty} I_m(\sigma) I_{-2m}(4\sigma h)} \end{aligned}$$

and

$$\langle \cos \phi \rangle_0 = \frac{\sum_{m=-\infty}^{\infty} I_m(\sigma) [I_{-2m+1}(4\sigma h) + I_{-2m-1}(4\sigma h)]}{2 \sum_{m=-\infty}^{\infty} I_m(\sigma) I_{-2m}(4\sigma h)}$$

B.3. Brownian Particle in a Tilted Periodic Potential

By introducing the column vectors $\mathbf{C}_n(k, t')$ defined as [14,16]

$$\mathbf{C}_n(k, t') = \begin{pmatrix} \vdots \\ c_{n-1,-1}(k, t') \\ c_{n-1,0}(k, t') \\ c_{n-1,1}(k, t') \\ \vdots \end{pmatrix}, \quad n = 1, 2, 3, \dots$$

Equation (262) can be written in the vector tridiagonal form

$$\frac{d}{dt'} \mathbf{C}_n(k, t') = \mathbf{Q}_n^-(k) \mathbf{C}_{n-1}(k, t') - \beta'(n-1) \mathbf{C}_n(k, t') + \mathbf{Q}_n^+(k) \mathbf{C}_{n+1}(k, t') \quad (\text{B4})$$

where the matrix elements of the infinite tridiagonal matrices \mathbf{Q}_n^- and \mathbf{Q}_n^+ are given by

$$[\mathbf{Q}_n^\pm]_{q,p} = i \sqrt{\frac{2n-1 \pm 1}{4}} \left[(q+k) \delta_{qp} \mp \frac{g}{4} (\delta_{qp-1} - \delta_{qp+1}) \right]$$

($-\infty < p, r < +\infty$). By Laplace transformation, Eq. (B4) can be rearranged as the set of matrix *three-term* recurrence equations

$$[\eta s + \beta'(n-1)] \tilde{\mathbf{C}}_n(k, s) - \mathbf{Q}_n^+(k) \tilde{\mathbf{C}}_{n+1}(k, s) - \mathbf{Q}_n^-(k) \tilde{\mathbf{C}}_{n-1}(k, s) = \delta_{n,1} \mathbf{C}_1(k, 0) \quad (\text{B5})$$

The exact solution of Eq. (B5) for the spectrum $\tilde{\mathbf{C}}_1(k, s)$ is given by (in terms of a matrix continued fraction)

$$\tilde{\mathbf{C}}_1(k, s) = \Delta_1(k, s) \mathbf{C}_1(k, 0) \quad (\text{B6})$$

where the matrix continued fraction $\Delta_n(k, s)$ is defined by the recurrence equation

$$\Delta_n(k, s) = \left\{ [\eta s + \beta'(n-1)] \mathbf{I} - \mathbf{Q}_n^+(k) \Delta_{n+1}(k, s) \mathbf{Q}_{n+1}^-(k) \right\}^{-1}$$

and \mathbf{I} is the unit matrix. Having determined $\tilde{\mathbf{C}}_1(k, s)$ and because of Eq. (263), one can calculate the dynamic structure factor $\tilde{S}(k, \omega)$ as

$$\tilde{S}(k, \omega) = (2\pi)^{-1} \mathbf{Z} \mathbf{C}_1^\dagger(k, 0) \Delta_1(k, i\omega) \mathbf{C}_1(k, 0) \quad (\text{B7})$$

where the symbol “ \dagger ” designates transformation of the column vector $\mathbf{C}_1(k, 0)$ to row vector and its conjugation.

B.4. Quantum Brownian Particle in a Double-Well Potential

Noting that the recurrence equation (457) may be separated into two independent systems with $q + n$ even and odd, we introduce the column vectors

$$\mathbf{C}_{2n-1}(t) = \begin{pmatrix} c_{2n-2,1}(t) \\ c_{2n-2,3}(t) \\ \vdots \end{pmatrix}, \quad \mathbf{C}_{2n}(t) = \begin{pmatrix} c_{2n-1,0}(t) \\ c_{2n-1,2}(t) \\ \vdots \end{pmatrix}, \quad (n \geq 1)$$

Now Eq. (457) can be rearranged as the set of matrix recurrence equations for the one-sided Fourier transforms $\mathbf{C}_n(t)$, namely,

$$\begin{aligned} \frac{d}{dt} \mathbf{C}_n(t') &= \mathbf{Q}_n^- \mathbf{C}_{n-1}(t') - \beta'(n-1) \mathbf{C}_n(t') + \mathbf{Q}_n^+ \mathbf{C}_{n+1}(t') \\ &\quad + \Lambda [\mathbf{q}_n \mathbf{C}_{n-2}(t') + \mathbf{r}_n \mathbf{C}_{n-3}(t')] \end{aligned} \quad (\text{B8})$$

where \mathbf{r}_n , \mathbf{q}_n , and \mathbf{Q}_n^\pm are two-, three-, and four-diagonal matrices, respectively. Their matrix elements are given by

$$\begin{aligned} [\mathbf{Q}_{2n-m}^\pm]_{p,q} &= \pm \sqrt{2n-m - \frac{1 \mp 1}{2}} \\ &\times \left(\delta_{pq+2-m} e_{2p-5+m} + \delta_{pq+1-m} d_{2p-3+m}^\pm + \delta_{pq-m} d_{2p-2+m}^\mp + \delta_{pq-1-m} e_{2p-2+m} \right) \\ [\mathbf{q}_{2n-m}]_{p,q} &= \beta' \sqrt{(2n-1-m)(2n-2-m)} \\ &\quad \times \left(\delta_{pq+1} h_{2p-4+m} + \delta_{pq} g_{2p-2+m} + \delta_{pq-1} h_{2p-2+m} \right) \\ [\mathbf{r}_{2n-m}]_{p,q} &= \sqrt{(2n-1-m)(2n-2-m)(2n-3-m)} \\ &\quad \times \left(f_{2p-3+m} \delta_{pq+1-m} + f_{2p-2+m} \delta_{pq-m} \right) \end{aligned}$$

where $m = 0, 1$,

$$\begin{aligned} d_q^\pm &= \frac{\alpha^{-3} B^{1/4}}{2} \sqrt{q+1} \left[3(q+1) - 2\alpha^2 \sqrt{Q} \pm \alpha^4 \right] \\ e_q &= \frac{B^{1/4} \alpha^{-3}}{2} \sqrt{(q+3)(q+2)(q+1)} \\ f_q &= 12B^{3/4} \alpha^{-1} \sqrt{q+1} \\ h_q &= 12\alpha^{-2} \sqrt{B(q+2)(q+1)} \\ g_q &= 4\sqrt{B} \left[3\alpha^{-2}(2q+1) - 2\sqrt{Q} \right] \end{aligned}$$

Next, we use perturbation theory to find the solution of Eq. (B8) as

$$\mathbf{C}_n(t') = \mathbf{C}_n^0(t') + \Lambda \mathbf{C}_n^1(t') \quad (\text{B9})$$

treating Λ as the customary small parameter. Substituting Eq. (B9) into Eq. (B8), we have in the zero order of perturbation theory the matrix three-term differential–recurrence relation

$$\frac{d}{dt'} \mathbf{C}_n^0(t') = \mathbf{Q}_n^- \mathbf{C}_{n-1}^0(t') - \beta'(n-1) \mathbf{C}_n^0(t') + \mathbf{Q}_n^+ \mathbf{C}_{n+1}^0(t')$$

and in the first order of perturbation theory the forced three-term matrix differential–recurrence relation

$$\frac{d}{dt'} \mathbf{C}_n^1(t') = \mathbf{Q}_n^- \mathbf{C}_{n-1}^1(t') - \beta'(n-1) \mathbf{C}_n^1(t') + \mathbf{Q}_n^+ \mathbf{C}_{n+1}^1(t') + \mathbf{R}_n(t')$$

where $\mathbf{R}_n(t') = \mathbf{q}_n \mathbf{C}_{n-2}^0(t') + \mathbf{r}_n \mathbf{C}_{n-3}^0(t')$.

By invoking the general method [14,16] for solving three-term matrix recursion equations, we have the exact solution for the zero-order spectrum $\tilde{\mathbf{C}}_n^0(s) = \int_0^\infty \mathbf{C}_n^0(t) e^{-st} dt$ in terms of a matrix continued fraction, namely,

$$\begin{aligned} \tilde{\mathbf{C}}_1^0(s) &= \mathbf{\Delta}_1(s) \mathbf{C}_1^0(0) \\ \tilde{\mathbf{C}}_n^0(s) &= \mathbf{S}_n^- \mathbf{C}_{n-1}^0(s) = \mathbf{S}_n^- \mathbf{S}_{n-1}^- \dots \mathbf{S}_2^- \mathbf{\Delta}_1(s) \mathbf{C}_1^0(0) \end{aligned}$$

where $\mathbf{S}_n^- = \mathbf{\Delta}_n(s) \mathbf{Q}_n^-$ and the matrix continued fraction $\mathbf{\Delta}_n(s)$ is defined by the recurrence equation

$$\mathbf{\Delta}_n(s) = \left\{ [s + \beta'(n-1)] \mathbf{I} - \mathbf{Q}_n^+ \mathbf{\Delta}_{n+1}(s) \mathbf{Q}_{n+1}^- \right\}^{-1}$$

In like manner, we also have the exact solution for the first-order spectrum $\tilde{\mathbf{C}}_1^1(s)$ in terms of a matrix continued fraction, namely,

$$\tilde{\mathbf{C}}_1^1(s) = \mathbf{\Delta}_1(s) \left\{ \mathbf{C}_1^1(0) + \mathbf{S}_2^+ \mathbf{S}_3^+ [\mathbf{C}_3^1(0) + \mathbf{F}] \right\}$$

where $\mathbf{S}_n^+ = \mathbf{Q}_{n-1}^+ \mathbf{\Delta}_n(s)$ and

$$\begin{aligned} \mathbf{F} &= \left\{ \mathbf{q}_3 + \mathbf{S}_4^+ \left[\mathbf{q}_4 \mathbf{S}_2^- + \mathbf{r}_4 + \sum_{n=5}^{\infty} \mathbf{S}_5^+ \dots \mathbf{S}_n^+ (\mathbf{q}_n \mathbf{S}_{n-2}^- + \mathbf{r}_n) \mathbf{S}_{n-3}^- \dots \mathbf{S}_2^- \right] \right\} \\ &\quad \times \mathbf{\Delta}_1(s) \mathbf{C}_1^0(0) \end{aligned}$$

because in the first order of perturbation theory, the only nonzero initial conditions are $\mathbf{C}_1^0(0)$, $\mathbf{C}_1^1(0)$, and $\mathbf{C}_3^1(0)$ [as dictated by the Wigner distribution equations (451)]

and (455)]. Thus, the only nonzero initial conditions $c_{m,2p+1}(0) = c_{m,2p+1}^0(0) + \Lambda c_{m,2p+1}^1(0)$ with $c_{m,2p+1}^k(0)$ ($m = 0, 2$ and $k = 0, 1$) given by

$$c_{m,2p+1}^k(0) = \frac{\int_{-\infty}^{\infty} \xi F_m^k(\xi) H_{2p+1}(\alpha\xi) e^{-(\alpha^2\xi^2 - 2\sqrt{Q}\xi^2 + \xi^4)/2} d\xi}{Z_{cl} \sqrt{2^{2p+1}(2p+1)!B}}$$

where

$$F_0^0(\xi) = 1, F_2^0(\xi) = 0$$

$$F_0^1(\xi) = 16 \left[\xi^2(-\sqrt{Q} + \xi^2)^2 + \sqrt{Q} - 2\xi^2 \right] - \frac{Z_1}{Z_{cl}\sqrt{B}}$$

$$F_2^1(\xi) = 4\sqrt{2} \left(3\xi^2 - \sqrt{Q} \right)$$

$$Z_{cl} = \int_{-\infty}^{\infty} e^{-V(x')} dx' = \sqrt{\pi}(2B)^{-1/4} D_{-1/2} \left(-\sqrt{2Q} \right) e^{Q/2}$$

and

$$\begin{aligned} \frac{Z_1}{\sqrt{B}Z_{cl}} &= \frac{1}{\sqrt{B}Z_{cl}} \int_{-\infty}^{\infty} \left(V'(x')^2 - V''(x') \right) e^{-V(x')} dx' \\ &= -\sqrt{8} \left[D_{1/2} \left(-\sqrt{2Q} \right) + D_{-3/2} \left(-\sqrt{2Q} \right) \right] / D_{-1/2} \left(-\sqrt{2Q} \right) \end{aligned}$$

B.5. Quantum Brownian Particle in a Periodic Potential

First we introduce the column vectors

$$\mathbf{C}_n(t) = \begin{pmatrix} \vdots \\ c_{n-1,-1}(k, t') \\ c_{n-1,0}(k, t') \\ c_{n-1,1}(k, t') \\ \vdots \end{pmatrix}$$

Hence, the scalar multiterm recurrence equation (475) can be rearranged as the five-term matrix differential–recurrence relation

$$\begin{aligned} \frac{d}{dt} \mathbf{C}_n(t') &= \mathbf{Q}_n^- \mathbf{C}_{n-1}(t') - \beta'(n-1) \mathbf{C}_n(t') + \mathbf{Q}_n^+ \mathbf{C}_{n+1}(t') \\ &+ \Lambda \left[\mathbf{q}_n \mathbf{C}_{n-2}(t') + \mathbf{r}_n \mathbf{C}_{n-3}(t') \right] \end{aligned} \quad (\text{B10})$$

where the matrix elements of \mathbf{Q}_n^\pm , \mathbf{q}_n , \mathbf{r}_n are given by

$$\begin{aligned} [\mathbf{Q}_n^\pm]_{q,p} &= i\sqrt{\frac{2n-1\pm 1}{4}} \left[(q+k)\delta_{qp} \mp \frac{g}{4} (\delta_{qp-1} - \delta_{qp+1}) \right] \\ [\mathbf{r}_n]_{q,p} &= ig\sqrt{\frac{(n-1)(n-2)(n-3)}{8}} (\delta_{qp-1} - \delta_{qp+1}) \\ [\mathbf{q}_n]_{q,p} &= g\beta' \sqrt{(n-1)(n-2)} (\delta_{qp-1} + \delta_{qp+1}) \end{aligned}$$

and $\delta_{q,p}$ is Kronecker's delta. Next, we use perturbation theory to find the solution of Eq. (B10) treating Λ as the customary small parameter so that we seek a solution as

$$\mathbf{C}_n(t') = \mathbf{C}_n^0(t') + \Lambda \mathbf{C}_n^1(t') \quad (\text{B11})$$

Substituting Eq. (B11) into Eq. (B10), we have the matrix three-term differential–recurrence relation for $\mathbf{C}_n^0(t')$ in the zero order of perturbation theory

$$\frac{d}{dt'} \mathbf{C}_n^0(t') = \mathbf{Q}_n^- \mathbf{C}_{n-1}^0(t') - \beta'(n-1) \mathbf{C}_n^0(t') + \mathbf{Q}_n^+ \mathbf{C}_{n+1}^0(t')$$

and in the first order of perturbation theory the forced matrix three-term differential–recurrence relation for $\mathbf{C}_n^1(t')$, namely,

$$\frac{d}{dt'} \mathbf{C}_n^1(t') = \mathbf{Q}_n^- \mathbf{C}_{n-1}^1(t') - \beta'(n-1) \mathbf{C}_n^1(t') + \mathbf{Q}_n^+ \mathbf{C}_{n+1}^1(t') + \mathbf{R}_n(t')$$

where $\mathbf{R}_n(t') = \mathbf{q}_n \mathbf{C}_{n-2}^0(t') + \mathbf{r}_n \mathbf{C}_{n-3}^0(t')$.

By invoking the general method [14,16] for solving three-term matrix recursion equations, we have the exact solution for the zero-order spectrum $\tilde{\mathbf{C}}_n^0(s) = \int_0^\infty \mathbf{C}_n^0(t) e^{-st} dt$ in terms of a matrix continued fraction, namely,

$$\begin{aligned} \tilde{\mathbf{C}}_1^0(s) &= \mathbf{\Delta}_1(s) \mathbf{C}_1^0(0) \\ \tilde{\mathbf{C}}_n^0(s) &= \mathbf{S}_n^- \mathbf{C}_{n-1}^0(s) = \mathbf{S}_n^- \mathbf{S}_{n-1}^- \dots \mathbf{S}_2^- \mathbf{\Delta}_1(s) \mathbf{C}_1^0(0) \end{aligned}$$

where $\mathbf{S}_n^- = \mathbf{\Delta}_n(s) \mathbf{Q}_n^-$ and the matrix continued fraction $\mathbf{\Delta}_n(k, s)$ is defined by the recurrence equation

$$\mathbf{\Delta}_n(s) = \left\{ [s + \beta'(n-1)] \mathbf{I} - \mathbf{Q}_n^+ \mathbf{\Delta}_{n+1}(s) \mathbf{Q}_{n+1}^- \right\}^{-1}$$

In like manner, we also have the exact solution for the first-order spectrum $\tilde{\mathbf{C}}_1^1(k, s)$ in terms of a matrix continued fraction, namely,

$$\tilde{\mathbf{C}}_1^1(s) = \mathbf{\Delta}_1(s) \mathbf{C}_1^1(0) + \mathbf{\Delta}_1(s) \mathbf{S}_2^+ \mathbf{S}_3^+ [\mathbf{C}_3^1(0) + \mathbf{F}]$$

where $\mathbf{S}_n^+ = \mathbf{Q}_{n-1}^+ \mathbf{\Delta}_n(s)$ and

$$\mathbf{F} = \left[\mathbf{q}_3 + \sum_{n=4}^{\infty} \mathbf{S}_4^+ \dots \mathbf{S}_n^+ (\mathbf{q}_n \mathbf{S}_{n-2}^- + \mathbf{r}_n) \mathbf{S}_{n-3}^- \dots \mathbf{S}_2^- \right] \mathbf{\Delta}_1(s) \mathbf{C}_1^0(0)$$

Here, we have noted that $\mathbf{C}_n^0(0) = 0$, $n \geq 2$ and $\mathbf{C}_2^1(0) = \mathbf{0}$, $\mathbf{C}_n^1(0) = \mathbf{0}$, $n \geq 4$.

The initial condition vectors $\mathbf{C}_n^0(0)$ and $\mathbf{C}_n^1(0)$ can be calculated just as in the classical case [16] by using the initial condition at $t=0$ for $W(x', p', x'_0, p'_0, 0) = W_{st}(x'_0, p'_0)$, Eq. (477). However, instead of the Maxwell–Boltzmann distribution of the classical theory, the equilibrium Wigner distribution function $W_{st}(x'_0, p'_0)$ now has the form [174,175]

$$W_{st}(x'_0, p'_0) = Z^{-1} e^{-p_0'^2 - U(x'_0)} \left\{ 1 + \Lambda \left[U'^2(x'_0) + (2p_0'^2 - 3) U''(x'_0) \right] \right\}$$

where the partition function Z is given by

$$\begin{aligned} Z &= \sqrt{\pi} \int_0^{2\pi} \left\{ 1 + \Lambda (U'(x'_0))^2 - 2\Lambda U''(x'_0) \right\} e^{-U(x'_0)} dx'_0 \\ &= Z_{cl} \left[1 - \Lambda g I_1(g) / I_0(g) \right] \end{aligned}$$

Here, $Z_{cl} = 2\pi^{3/2} I_0(g)$ is the classical partition function and $I_0(x)$ and $I_1(x)$ are modified Bessel functions of the first kind. Equations (473), (474), and (477) yield the initial conditions for $c_{n,q}(t)$ as

$$c_{n,q}(0) = \frac{1}{\sqrt{2^n n!}} \left\langle H_n(p'_0) e^{iqx'_0 + U(x'_0)/2} \right\rangle_0$$

where the brackets $\langle \rangle_0$ mean the average over $W_{st}(x'_0, p'_0)$. By representing $c_{n,q}(0)$ via perturbation theory as $c_{n,q}(0) = c_{n,q}^0(0) + \Lambda c_{n,q}^1(0)$, we have the initial conditions for $c_{n,q}^0(0)$ and $c_{n,q}^1(0)$, namely,

$$\begin{aligned} c_{0,q}^0(0) &= \sqrt{\pi} Z_{cl}^{-1} \int_0^{2\pi} e^{iqx'_0 - U(x'_0)/2} dx'_0 = 2\pi^{3/2} Z_{cl}^{-1} I_{|q|}(g/2) \\ c_{0,q}^1(0) &= \sqrt{\pi} Z_{cl}^{-1} \int_0^{2\pi} \left[U'^2(x'_0) - 2U''(x'_0) + \frac{gI_1(g)}{I_0(g)} \right] e^{iqx'_0 - U(x'_0)/2} dx'_0 \\ &= -2\pi^{3/2} Z_{cl}^{-1} \left[4q^2 - g \frac{I_1(g)}{I_0(g)} \right] I_{|q|}(g/2) \\ c_{2,q}^1(0) &= \sqrt{2\pi} Z_{cl}^{-1} \int_0^{2\pi} U''(x') e^{iqx'_0 - U(x'_0)/2} dx'_0 = \frac{g}{\sqrt{2}} \left[c_{0,q+1}^0(0) + c_{0,q-1}^0(0) \right] \end{aligned}$$

Having determined $\tilde{\mathbf{C}}_1(k, s) = \tilde{\mathbf{C}}_1^0(s) + \Lambda \tilde{\mathbf{C}}_1^1(s)$, we can evaluate the dynamic structure factor $\tilde{S}(k, \omega)$ in terms of $\tilde{c}_{n,q}(k, \omega)$ as

$$\tilde{S}(k, \omega) = \frac{Z_{cl}}{2\pi^{3/2}} \sum_{q=-\infty}^{\infty} c_{0,q}^0(0) \tilde{c}_{0,q}(k, \omega)$$

APPENDIX C: EVALUATION OF AVERAGES IN THE UNDAMPED LIMIT

C.1. Fixed Axis Rotator in a Symmetrical Double-Well Potential

In the very low damping limit ($\beta' \ll 1$), the energy of the dipole is not conserved but will vary very slowly with time (quasistationary). Thus, the dynamics of the system are described by the one-dimensional Fokker–Planck equation (179) (also derived by Stratonovich [187]) and differ but little from those of the undamped limit ($\beta' = 0$). In the undamped limit (when the Langevin torque in Eq. (134) vanishes), the energy ε , Eq. (178), is a constant of the motion. Thus, the dynamics of the dipole are described by the deterministic nonlinear differential equation

$$\eta \frac{d}{dt} \phi(t) = \pm \sqrt{\varepsilon + 2\sigma \sin^2 \phi(t)}$$

This equation has a solution [188] in terms of the Jacobian doubly periodic elliptic function $\text{cn}(u|m)$ and $\text{dn}(u|m)$ [72]

$$\sin \phi(t) = \begin{cases} \pm \text{dn} \left(\frac{t}{\eta} \sqrt{2\sigma} + w \middle| m(\varepsilon) \right), & -2\sigma \leq \varepsilon < 0 \\ \pm \text{cn} \left(\frac{t}{\eta} \sqrt{\varepsilon + 2\sigma} + w \sqrt{m(\varepsilon)} \middle| m^{-1}(\varepsilon) \right), & 0 \leq \varepsilon < \infty \end{cases} \quad (\text{C1})$$

where

$$w = \int_0^{\phi(0)} \left[1 - m(\varepsilon) \sin^2 x \right]^{-1/2} dx, \quad m(\varepsilon) = 1 + \varepsilon/2\sigma$$

Because [72]

$$\text{sn}^2(u|m) + \text{cn}^2(u|m) = 1 \quad \text{and} \quad m \text{sn}^2(u|m) + \text{dn}^2(u|m) = 1 \quad (\text{C2})$$

we have

$$\sin^2 \phi(t) = \begin{cases} 1 - m(\varepsilon) \operatorname{sn}^2 \left(\frac{t}{\eta} \sqrt{2\sigma} + w \middle| m(\varepsilon) \right), & -2\sigma \leq \varepsilon < 0 \\ 1 - \operatorname{sn}^2 \left(\frac{t}{\eta} \sqrt{\varepsilon + 2\sigma} + w \sqrt{m(\varepsilon)} \middle| m^{-1}(\varepsilon) \right), & 0 \leq \varepsilon < \infty \end{cases} \quad (\text{C3})$$

In order to proceed, we recall the Fourier series for the Jacobian functions [189]

$$\operatorname{cn}(u|m) = \frac{2\pi}{m^{1/2} K(m)} \sum_{n=0}^{\infty} \frac{q^{n+1/2}}{1+q^{2n+1}} \cos \left[\frac{(2n+1)\pi u}{2K(m)} \right] \quad (\text{C4})$$

$$\operatorname{dn}(u|m) = \frac{\pi}{2K(m)} + \frac{2\pi}{K(m)} \sum_{n=1}^{\infty} \frac{q^n}{1+q^{2n}} \cos \left[\frac{n\pi u}{K(m)} \right] \quad (\text{C5})$$

$$m \operatorname{sn}^2(u|m) = 1 - \frac{E(m)}{K(m)} - \frac{2\pi^2}{K^2(m)} \sum_{n=1}^{\infty} \frac{nq^n}{1-q^{2n}} \cos \left[\frac{n\pi u}{K(m)} \right] \quad (\text{C6})$$

where $q = \exp[-\pi K(1-m)/K(m)]$, $K(m)$ and $E(m)$ are complete elliptic integrals of the first and second kind. Thus, from Eqs. (C3)–(C6), we have $\overline{\overline{\sin \phi}}$ and $\overline{\overline{\sin^2 \phi}}$ averaged over the phase w , namely,

$$\overline{\overline{\sin \phi(\varepsilon, w)}} = \frac{1}{4K} \int_{-2K}^{2K} \sin \phi(\varepsilon, w) dw = \begin{cases} \pm \pi/2K [m(\varepsilon)], & -2\sigma \leq \varepsilon < 0 \\ 0, & 0 \leq \varepsilon < \infty \end{cases} \quad (\text{C7})$$

$$\overline{\overline{\sin^2 \phi(\varepsilon, w)}} = \frac{1}{4K} \int_{-2K}^{2K} \sin^2 \phi(\varepsilon, w) dw = \begin{cases} \frac{E[m(\varepsilon)]}{K[m(\varepsilon)]}, & -2\sigma \leq \varepsilon < 0 \\ 1 - m(\varepsilon) \left\{ 1 - \frac{E[m^{-1}(\varepsilon)]}{K[m^{-1}(\varepsilon)]} \right\}, & 0 \leq \varepsilon < \infty \end{cases} \quad (\text{C8})$$

Accordingly, because W_{st} is the equilibrium Maxwell–Boltzmann distribution W_0 , namely,

$$W_0 [\phi(0), \dot{\phi}(0)] d\phi(0) d\dot{\phi}(0) = \frac{\eta e^{-\sigma}}{2\pi^{3/2} I_0(\sigma)} e^{-\eta^2 \dot{\phi}^2(0) + 2\sigma \sin^2 \phi(0)} d\phi(0) d\dot{\phi}(0)$$

by making the transformation of the variables $\{\phi(0), \dot{\phi}(0)\} \rightarrow \{w, \varepsilon\}$ [188], and by integrating the distribution function $W_0(\varepsilon)$ over the phase w , we have

$$W_0(\varepsilon) d\varepsilon = \frac{\sqrt{2}e^{-\sigma}}{\pi^{3/2}\sigma^{1/2}I_0(\sigma)} \text{Re}\{K[m(\varepsilon)]\} e^{-\varepsilon} d\varepsilon, \quad \int_{-2\sigma}^{\infty} W_0(\varepsilon) d\varepsilon = 1 \quad (\text{C9})$$

The average of a dynamical quantity $\overline{A(\varepsilon, w)}$ is defined as

$$\begin{aligned} \langle \overline{A} \rangle_0 &= \int_{-2\sigma}^{\infty} \overline{A}(\varepsilon) W_0(\varepsilon) d\varepsilon \\ &= \frac{\sqrt{2}e^{-\sigma}}{\pi^{3/2}\sigma^{1/2}I_0(\sigma)} \left[\int_{-2\sigma}^0 \overline{A}(\varepsilon) K[m(\varepsilon)] e^{-\varepsilon} d\varepsilon \right. \\ &\quad \left. + \int_0^{\infty} \frac{1}{\sqrt{1+\varepsilon/2\sigma}} \overline{A}(\varepsilon) K[m^{-1}(\varepsilon)] e^{-\varepsilon} d\varepsilon \right] \end{aligned} \quad (\text{C10})$$

In particular, we have from Eqs. (C8) and (C10)

$$\langle \overline{\sin^2 \phi} \rangle_0 = \int_{-2\sigma}^{\infty} \overline{\sin^2 \phi}(\varepsilon) W_0(\varepsilon) d\varepsilon = \frac{\sqrt{2}e^{-\sigma}}{\pi^{3/2}\sigma^{1/2}I_0(\sigma)} \int_{-2\sigma}^{\infty} \text{Re}\{E[m(\varepsilon)]\} e^{-\varepsilon} d\varepsilon \quad (\text{C11})$$

Equation (C11) yields the same equilibrium value as Eq. (177). One can also verify that the equipartition theorem, namely,

$$\eta^2 \langle \overline{\dot{\phi}^2} \rangle_0 = \langle \varepsilon + 2\sigma \overline{\sin^2 \phi} \rangle_0 = \frac{1}{2} \quad (\text{C12})$$

also holds. By using Eqs. (C7)–(C11), we have Eq. (180).

The longitudinal correlation function $C(t) = \langle \sin \phi(0) \sin \phi(t) \rangle_0$ for the undamped rotation can be derived from Eqs. (C2), (C4), (C5), and (C9) and is

given by

$$C(t) = \frac{4\sqrt{2\pi/\sigma}}{I_0(\sigma) + I_1(\sigma)} \left\{ \int_{-2\sigma}^0 \left(\frac{1}{8} + \sum_{n=1}^{\infty} \frac{q^{2n}}{(1+q^{2n})^2} \cos \left[\frac{n\pi\sqrt{2\sigma}}{\eta K[m(\varepsilon)]} t \right] \right) \frac{e^{-\varepsilon-\sigma}}{K[m(\varepsilon)]} d\varepsilon \right. \\ \left. + \int_0^{\infty} \frac{m^{1/2}(\varepsilon) e^{-\varepsilon-\sigma}}{K[m^{-1}(\varepsilon)]} \sum_{n=1}^{\infty} \frac{q^{2n-1}}{(1+q^{2n-1})^2} \cos \left[\frac{(2n-1)\pi\sqrt{\varepsilon+2\sigma}}{2\eta K[m^{-1}(\varepsilon)]} t \right] d\varepsilon \right\} \quad (C13)$$

For $\sigma=0$, $C(t)$ from Eq. (C13) reduces to the free rotator correlation function, namely,

$$C(t) = \frac{1}{\sqrt{\pi}} \int_0^{\infty} \frac{1}{\sqrt{\varepsilon}} \cos(\sqrt{\varepsilon}t/\eta) e^{-\varepsilon} d\varepsilon = e^{-t^2/4\eta^2} \quad (C14)$$

Equation (C14) yields $\tau_{\parallel} = \eta\sqrt{\pi}$.

C.2. Fixed Axis Rotator in an Asymmetrical Double-Well Potential

In the very low damping limit ($\beta' \ll 1$), the energy of the dipole is again not conserved but will vary very slowly with time (quasistationary). Thus, the dynamics of the system are described by the one-dimensional Fokker–Planck equation (205) and differ but little from those of the undamped limit ($\beta' = 0$). In the undamped limit, the energy ε is a constant of the motion. Thus, the dynamics of the dipole are described by the deterministic differential equation

$$\left(\eta \frac{d\phi}{dt} \right)^2 = \varepsilon + 4\sigma h \cos \phi + 2\sigma \cos^2 \phi$$

or, by introducing a new variable $Z = \cos \phi$,

$$\left(\eta \frac{dZ}{dt} \right)^2 = 2\sigma \left(Z^2 + 2hZ + \varepsilon' \right) \left(1 - Z^2 \right) \quad (C15)$$

where $\varepsilon' = \varepsilon/(2\sigma)$. Equation (C15) has a solution [189,190] in terms of the Jacobian doubly periodic elliptic functions $\text{sn}(u|m)$ and $\text{cn}(u|m)$ [72]:

$$\cos \phi(t) = \begin{cases} \pm \frac{1 - a^{\pm} \text{sn}^2(M_1 t/\eta + w^{\pm}, m_1)}{1 + a^{\pm} \text{sn}^2(M_1 t/\eta + w^{\pm}, m_1)}, & -1 \mp 2h \leq \varepsilon' \leq h^2 \\ -\frac{a - \text{cn}(M_2 t/\eta + w, m_2)}{1 - a \text{cn}(M_2 t/\eta + w, m_2)}, & \varepsilon' \geq h^2 \end{cases} \quad (C16)$$

where

$$\begin{aligned}
m_1 &= \frac{1 - \varepsilon' - 2\sqrt{h^2 - \varepsilon'}}{1 - \varepsilon' + 2\sqrt{h^2 - \varepsilon'}}, & m_2 &= \frac{1}{2} \left(1 + \frac{1 - \varepsilon'}{\sqrt{(1 + \varepsilon')^2 - 4h^2}} \right) \\
m_1 &= \frac{1 - \varepsilon' - 2\sqrt{h^2 - \varepsilon'}}{1 - \varepsilon' + 2\sqrt{h^2 - \varepsilon'}}, & m_2 &= \frac{1}{2} \left(1 + \frac{1 - \varepsilon'}{\sqrt{(1 + \varepsilon')^2 - 4h^2}} \right) \\
M_1 &= \sqrt{\sigma \left(1 - \varepsilon' + 2\sqrt{h^2 - \varepsilon'} \right) / 2}, & M_2 &= \sqrt{2\sigma \sqrt{(1 + \varepsilon')^2 - 4h^2}} \\
a^\pm &= \frac{1 \pm h - \sqrt{h^2 - \varepsilon'}}{1 \mp h + \sqrt{h^2 - \varepsilon'}}, & a &= \frac{2h}{1 + \varepsilon' + \sqrt{(1 + \varepsilon')^2 - 4h^2}} \\
w^\pm &= \int_0^{\sqrt{\frac{1 \mp \cos \phi(0)}{a^\pm(1 \pm \cos \phi(0))}}} \frac{dt}{\sqrt{(1 - t^2)(1 - m_1 t^2)}}, \\
w &= \int_0^{\frac{\sin \phi(0) \sqrt{1 - a^2}}{1 + a \cos \phi(0)}} \frac{dt}{\sqrt{(1 - t^2)(1 - m_2 t^2)}}
\end{aligned}$$

We remark that the three solutions given by Eq. (C16) correspond to the three possible domains of energy variations, namely, the oscillations in the deeper well (domain I: $-1 - 2h \leq \varepsilon' \leq h^2$), the oscillations in the shallow well (domain II: $-1 - 2h \leq \varepsilon' \leq h^2$), and rotation (domain II: $h^2 \leq \varepsilon' < \infty$). The condition for the existence of two wells is $h < 1$.

The function $\cos \phi(t)$ is a periodic function of its arguments $M_1 t / \eta + w^\pm$ and $M_2 t / \eta + w$ with the period T given by $2K(m_1)$ for $-1 \mp 2h \leq \varepsilon' \leq h^2$ and $4K(m_2)$ for $\varepsilon' \geq h^2$, where $K(m)$ is the complete elliptic integral of the first kind. Hence, $\cos \phi(t)$ can be expanded in the Fourier series

$$\cos \phi(t') = \frac{1}{2} c_0 + \sum_{n=1}^{\infty} c_n \cos \left(\frac{2\pi n(t' + w)}{T} \right) \quad (\text{C17})$$

with coefficients

$$c_n = \frac{2}{T} \int_{-T/2}^{T/2} \cos \phi(t') e^{-2i\pi n t' / T} dt'$$

Thus, we can readily obtain $\cos \phi$ averaged over the phase w from Eq. (C17), namely,

$$\overline{\overline{\cos \phi(\varepsilon, w)}} = \frac{1}{T} \int_{-T/2}^{T/2} \cos \phi(\varepsilon, w) dw = \frac{1}{2} c_0$$

The coefficients c_0 can be calculated analytically using tables of integrals from Ref. [191]. We have

$$\overline{\overline{\cos \phi(\varepsilon)}} = \begin{cases} \mp 1 \pm 2 \frac{\Pi(-a^\pm, m_1)}{K(m_1)} & -1 \mp 2h \leq \varepsilon' \leq h^2 \\ -\frac{1}{a} + \frac{(1-a^2)}{aK(m_2)\sqrt{1-m_2}} \Pi\left(a^2, \frac{m_2}{m_2-1}\right) & \varepsilon' \geq h^2 \end{cases} \quad (\text{C18})$$

and

$$\overline{\overline{\cos^2 \phi(\varepsilon)}} = \begin{cases} \frac{a^\pm - 1}{a^\pm + 1} + 2 \frac{a^\pm E(m_1) - [(a^\pm)^2 - m_1] \Pi(-a^\pm, m_1)}{(a^\pm + 1)(a^\pm + m_1)K(m_1)} & -1 \mp 2h \leq \varepsilon' \leq h^2 \\ 1 + \frac{E(m_2) - \Pi\left(a^2, \frac{m_2}{m_2-1}\right) / \sqrt{1-m_2}}{[m_2 + a^2/(1-a^2)] K(m_2)} & \varepsilon' \geq h^2 \end{cases} \quad (\text{C19})$$

where $E(m)$ and $\Pi(v, m)$ are complete elliptic integrals of the second and the third kind, respectively.

Hence, because W_{st} is the equilibrium Maxwell–Boltzmann distribution W_0 , namely,

$$W_0 [\phi(0), \dot{\phi}(0)] d\phi(0) d\dot{\phi}(0) = \frac{\eta e^{-\eta^2 \phi^2(0) + 2\sigma \cos^2 \phi(0) + 4\sigma h \cos \phi(0)}}{2\sqrt{\pi^3} e^\sigma \sum_{m=-\infty}^{\infty} I_m(\sigma) I_{-2m}(4\sigma h)} d\phi(0) d\dot{\phi}(0) \quad (\text{C20})$$

by making the transformation of the variables $\{\phi(0), \dot{\phi}(0)\} \rightarrow \{w, \varepsilon\}$ [188], and by integrating the distribution function W_0 over the phase w , we obtain

$$W_0(\varepsilon) d\varepsilon = \frac{e^{-\sigma - \varepsilon} d\varepsilon}{\pi^{3/2} \sum_{m=-\infty}^{\infty} I_m(\sigma) I_{-2m}(4\sigma h)} \begin{cases} K[m_1(\varepsilon)]/M_1(\varepsilon), & -1 \mp 2h \leq \varepsilon' \leq h^2 \\ 2K[m_2(\varepsilon)]/M_2(\varepsilon), & \varepsilon' \geq h^2 \end{cases} \quad (\text{C21})$$

The average of a dynamical quantity $\overline{\overline{A}}(\varepsilon)$ is defined as

$$\begin{aligned} \left\langle \overline{\overline{A}} \right\rangle_0 = & \frac{e^{-\sigma}}{\pi^{3/2} \sum_{m=-\infty}^{\infty} I_m(\sigma) I_{-2m}(4\sigma h)} \left[\int_{-2\sigma(1+2h)}^{2\sigma h^2} \overline{\overline{A}}(\varepsilon) K[m_1(\varepsilon)] M_1^{-1}(\varepsilon) e^{-\varepsilon} d\varepsilon \right. \\ & + \int_{-2\sigma(1-2h)}^{2\sigma h^2} \overline{\overline{A}}(\varepsilon) K[m_1(\varepsilon)] M_1^{-1}(\varepsilon) e^{-\varepsilon} d\varepsilon + 2 \int_{2\sigma h^2}^{\infty} \overline{\overline{A}}(\varepsilon) K[m_2(\varepsilon)] M_2^{-1}(\varepsilon) e^{-\varepsilon} d\varepsilon \left. \right] \end{aligned} \quad (\text{C22})$$

In particular, the equipartition theorem holds, namely,

$$\eta^2 \left\langle \overline{\overline{\dot{\phi}^2}} \right\rangle_0 = \left\langle \varepsilon + 2\sigma \overline{\overline{\cos^2 \phi}} + 4\sigma h \overline{\overline{\cos \phi}} \right\rangle_0 = \frac{1}{2}$$

C.3. Brownian Particle in a Double-Well Potential

In the very low damping limit ($\beta' \ll 1$), the energy of the particle is once more not conserved but will vary very slowly with time (quasistationary). Thus, the dynamics of the system are described by a one-dimensional Fokker–Planck equation (250) and differ but little from those of the undamped limit [$\beta' = 0$, when the Langevin torque in Eq. (212) vanishes]. The undamped limit has been treated in Refs [102,117,122]. We apply these results to evaluate integrals in Eq. (251). In the undamped limit, the energy ε , Eq. (249), is a constant of the motion, namely, $\dot{\varepsilon} = 0$. Equation (249) can be rearranged as the deterministic nonlinear differential equation describing the undamped dynamics of the particle

$$\frac{\eta}{\sqrt{e_2 B}} \frac{d}{dt} z(t) = \pm \sqrt{[z^2(t) - e_1/e_2][1 - z^2(t)]} \quad (\text{C23})$$

where $z(t) = y(t)/\sqrt{e_2}$ and $e_{1,2} = \sqrt{Q/B} (1 \mp \sqrt{1 + \varepsilon/Q})$ are the roots of the quadratic equation $\varepsilon + 2\sqrt{QB}x - Bx^2 = 0$. Equation (C23) has a solution [117,122] in terms of the Jacobian doubly periodic elliptic function $\text{cn}(u|m)$ and $\text{dn}(u|m)$ [72]

$$y(t) = \begin{cases} \pm \sqrt{e_2} \text{dn}(\sqrt{Be_2}t/\eta + w|m), & -Q \leq \varepsilon \leq 0 \\ \pm \sqrt{e_2} \text{cn}(\sqrt{B(e_2 - e_1)}t/\eta + w\sqrt{m}|m^{-1}), & 0 < \varepsilon < \infty \end{cases} \quad (\text{C24})$$

$$m = m(\varepsilon) = \frac{e_2 - e_1}{e_2} = \frac{2}{1 + (1 + \varepsilon/Q)^{-1/2}} \quad (\text{C25})$$

$$w = \int_{y(0)/\sqrt{e_2}}^1 \frac{1}{\sqrt{(x^2 - e_1/e_2)(1 - x^2)}} dx$$

By noting Eq. (C2), one has

$$y^2(t) = \begin{cases} e_2 [1 - m \operatorname{sn}^2(\sqrt{Be_2}t/\eta + w|m)], & -Q \leq \varepsilon \leq 0 \\ e_2 [1 - \operatorname{sn}^2(\sqrt{B(e_2 - e_1)}t/\eta + \sqrt{m}w|m^{-1})], & 0 < \varepsilon < \infty \end{cases} \quad (\text{C26})$$

Next, we recall Eqs. (C4)–(C6) and the Fourier series [189,192]

$$m^2 \operatorname{sn}^4(u|m) = \frac{1}{3} \left[2 + m - 2(1+m) \frac{E}{K} \right] + \frac{4\pi^2}{3K^2} \sum_{n=1}^{\infty} \left[\frac{n^2\pi^2}{4K^2} - m - 1 \right] \frac{nq^n}{1 - q^{2n}} \cos\left(\frac{n\pi u}{K}\right) \quad (\text{C27})$$

Thus, from Eqs. (C4)–(C6) and (C25)–(C29), we can obtain averages over the phase w averages $\overline{\overline{y}}$, $\overline{\overline{y^2}}$, and $\overline{\overline{y^4}}$. In particular, we have in the domain $-Q \leq \varepsilon \leq 0$

$$\overline{\overline{y}}(\varepsilon) = \frac{1}{K} \int_0^K y(\varepsilon, w) dw = \pm \pi \sqrt{e_2}/(2K) \quad (\text{C28})$$

$$\overline{\overline{y^2}}(\varepsilon) = e_2 E/K \quad (\text{C29})$$

$$\overline{\overline{y^4}}(\varepsilon) = \frac{e_2^2}{3} [m - 1 + (4 - 2m)E/K] \quad (\text{C30})$$

Accordingly, because W_{st} is the equilibrium Maxwell–Boltzmann distribution W_0 , namely,

$$W_0 [y(0), \dot{y}(0)] dy(0)d\dot{y}(0) = \frac{\eta}{Z\sqrt{\pi}} e^{-\eta^2 \dot{y}^2(0) + 2\sqrt{QB}y^2(0) - By^4(0)} dy(0)d\dot{y}(0)$$

by making the transformation of the variables $\{y(0), \dot{y}(0)\} \rightarrow \{w, \varepsilon\}$, and by integrating the distribution function $W_0(\varepsilon)$ over the phase w , we have

$$W_0(\varepsilon) d\varepsilon = \frac{2^{5/4} e^{-Q/2}}{\pi Q^{1/4} D_{-1/2}(-\sqrt{2Q})} \frac{\operatorname{Re}\{K[m(\varepsilon)]\} e^{-\varepsilon}}{\sqrt{1 + \sqrt{1 + \varepsilon/Q}}} d\varepsilon \quad (\text{C31})$$

The average of a dynamical quantity $\overline{\overline{X}}(\varepsilon)$ over ε is defined as

$$\langle \overline{\overline{X}} \rangle_0 = \int_{-Q}^{\infty} \overline{\overline{X}}(\varepsilon) W_0(\varepsilon) d\varepsilon, \quad \int_{-Q}^{\infty} W_0(\varepsilon) d\varepsilon = 1 \quad (\text{C32})$$

In particular, we have from Eqs. (C32) and (C33)

$$\langle \overline{\overline{y^2}} \rangle_0 = \frac{2^{11/4} Q^{1/4} e^{-Q/2}}{\pi D_{-3/2}(-\sqrt{2Q})} \int_{-Q}^{\infty} \sqrt{1 + \sqrt{1 + \varepsilon/Q} \operatorname{Re}[E(m)]} e^{-\varepsilon} d\varepsilon = 1 \quad (\text{C33})$$

Moreover, the equipartition theorem also holds, namely,

$$\eta^2 \langle \overline{\overline{\dot{y}^2}} \rangle_0 = \langle \varepsilon + 2\sqrt{QB} \overline{\overline{y^2}} - B \overline{\overline{y^4}} \rangle_0 = \frac{1}{2}$$

By using Eqs. (C26)–(C31) in Eq. (251) and noting that $\overline{\overline{y}}$ at $0 < \varepsilon < \infty$, we have

$$T^{VLD} \approx \frac{3\eta\pi^{3/2}}{4\beta' Z\sqrt{B}} \int_{-Q}^0 \frac{\sqrt{e_2} e^\varepsilon (e^Q - e^{-\varepsilon})^2}{[3\varepsilon + (1-m)Be_2^2] K + 2[3\sqrt{QB}e_2 - (2-m)Be_2^2] E} d\varepsilon \quad (\text{C34})$$

which after some simplifications leads to Eq. (252).

The correlation function $\langle y(0)y(t) \rangle_0$ for the undamped motion can be derived from Eqs. (C6), (C24), (C26), (C27), and (C31) and is given by [122] (in our notation)

$$\begin{aligned} \langle y(0)y(t) \rangle_0 = & \frac{2^{5/4}\pi e^{-Q/2}}{D_{-3/2}(-\sqrt{2Q})} \left\{ \int_{-Q}^0 \frac{(Q+\varepsilon)^{1/4}}{\sqrt{m}K(m)} \left(1 + 8 \sum_{n=1}^{\infty} \frac{q^{2n}}{(1+q^{2n})^2} \cos \left[\frac{n\pi\sqrt{Be_2}}{\eta K(m)} t \right] \right) e^{-\varepsilon} d\varepsilon \right. \\ & \left. + 8 \int_0^{\infty} \frac{(Q+\varepsilon)^{1/4}}{K(m^{-1})} \sum_{n=1}^{\infty} \frac{q^{2n-1}}{(1+q^{2n-1})^2} \cos \left[\frac{(2n-1)\pi\sqrt{B(e_2-e_1)}}{2\eta K(m^{-1})} t \right] e^{-\varepsilon} d\varepsilon \right\} \quad (\text{C35}) \end{aligned}$$

C.4. Brownian Particle in a Periodic Potential

For $\beta' \ll 1$, the dynamics of the system differ but little from those of the undamped limit ($\beta' = 0$) when the Langevin force vanishes. For $\beta' = 0$, the energy of the Brownian particles [see Eq. (283)] is a constant of the motion and so the dynamics

of the particle in the potential well are described by the following deterministic nonlinear differential equation

$$\dot{x}(t')^2 = \varepsilon + g \cos x(t')$$

or

$$\frac{d}{dt'} \cos x(t') = \pm \sqrt{[\varepsilon + g \cos x(t')][1 - \cos^2 x(t')]} \quad (\text{C36})$$

For $-g < \varepsilon < g$, Eq. (C36) has a solution in terms of the Jacobian doubly periodic elliptic function $\text{sn}(u|m)$ [189]:

$$\cos x(t') = 1 - 2m(\varepsilon) \text{sn}^2 \left(t' \sqrt{g/2} \pm w \mid m(\varepsilon) \right) \quad (\text{C37})$$

where

$$w = \int_0^{\arcsin(\sqrt{m(\varepsilon)} \sin[x(0)/2])} \left[1 - m(\varepsilon) \sin^2 x' \right]^{-1/2} dx' \quad (\text{C38})$$

$$m(\varepsilon) = \frac{g + \varepsilon}{2g} \quad (\text{C39})$$

Now we recall the Fourier series for $\text{sn}^2(u|m)$ Eq. (C6). Thus, we have from Eqs. (C37)–(C39)

$$\overline{\overline{\cos x}}(\varepsilon) = 2 \frac{E(m)}{K(m)} - 1 \quad (\text{C40})$$

where the double overbar denotes averaging over the fast phase variable, the dependence of the modulus m on ε is determined by Eq. (C39).

In order to evaluate equilibrium averages, one needs an equation for the stationary distribution function W_{st} . Because W_{st} is the equilibrium Maxwell–Boltzmann distribution W_0 , namely,

$$W_0 [x(0), \dot{x}(0)] dx(0) d\dot{x}(0) = \frac{1}{2\pi^{3/2} I_0(g)} e^{-\dot{x}^2(0) + g \cos x(0)} dx(0) d\dot{x}(0)$$

by making the transformation of the variables $\{x(0), \dot{x}(0)\} \rightarrow \{w, \varepsilon\}$, and by integrating the distribution function $W_0(\varepsilon)$ over the phase w , we have

$$W_0(\varepsilon) d\varepsilon = \begin{cases} \frac{K[m(\varepsilon)] e^{-\varepsilon}}{\pi^{3/2} I_0(g) \sqrt{g/2}} d\varepsilon, & (-g < \varepsilon < g) \\ \frac{\sqrt{2} K[m^{-1}(\varepsilon)] e^{-\varepsilon}}{\pi^{3/2} I_0(g) \sqrt{gm(\varepsilon)}} d\varepsilon, & (\varepsilon > g) \end{cases}$$

with $\int_{-g}^{\infty} W_0(\varepsilon) d\varepsilon = 1$. Because the diffusion coefficient $D^{(2)}$ in the Fokker–Planck equation (284) is defined by Eq. (285), the MFPT approach yields τ in the VLD limit

$$\frac{\tau}{\eta} \sim \frac{1}{4\beta'g} \int_{-g}^g \frac{\int_{-g}^{\varepsilon} e^{\varepsilon-x} K[m(x)] dx}{m(\varepsilon)K[m(\varepsilon)] + E[m(\varepsilon)]} d\varepsilon \quad (\text{C41})$$

APPENDIX D: ESCAPE RATE IN THE IHD LIMIT

In order to compare the exact numerical solution with the escape rate obtained from the Kramers theory [15], we adapt the procedure described for the intermediate to high damping classical case in [3,20]. In the IHD limit for the cosine potential given by Eq. (471) it is sufficient [8,9] to consider escape rate from a single well only. The escape rate considering an isolated well with a source of particles at point A (the bottom of the well) and a potential barrier at point C is then defined by

$$\Gamma^{\text{IHD}} = \frac{j_C}{n_A} = \frac{\int_{\text{top}} (p/m) W_{\text{st}}(x_C, p) dp}{\int_{\text{well}} W_{\text{st}}(x, p) dp dx} \quad (\text{D1})$$

Here, n_A is the number of particles in the bottom of a potential well at point A and j_C is the current across the barrier top at point C . The integrals in Eq. (D1) can be estimated via steepest descents by approximating the Wigner functions $W_{\text{st}}(x_C, p)$ and $W_{\text{st}}(x, p)$ [which are the equilibrium solutions of Eq. (472) near the points A and C] by those of the harmonic oscillator. The number of particles in the well n_A is given by

$$n_A \approx \int_{\text{well}} \int W_{\text{st}}(x, p) dx dp \approx \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_A(x, p) dx dp = \frac{\pi \hbar e^{-\beta V(x_A)}}{\sinh [\hbar \omega_A / (2k_B T)]} \quad (\text{D2})$$

where x_A is the bottom of the well. Here, we have approximated the Wigner function $W_{\text{st}}(x, p)$ [which is the equilibrium solution of Eq. (448) near the point A] by that of the harmonic oscillator, namely [168]

$$W_a(x, p) \approx \text{sech} [\hbar \omega_A / (2k_B T)] e^{-\beta V(x_A) - (p^2 + m^2 \omega_A^2 \bar{x}^2) \frac{\tanh[\hbar \omega_A / (2k_B T)]}{m \hbar \omega_A}}$$

where $\omega_A = \sqrt{V''(x_A)/m}$ and $\bar{x} = x - x_A$. In order to calculate the current j_C through the barrier at C , one needs the Wigner stationary solution *near the top* (point

C). Here, the Wigner function is approximated by that of the inverted harmonic oscillator potential, namely,

$$W(x', p') = e^{-\beta V(x_C)} \sec [\hbar\omega_C/(2k_B T)] e^{-m(p'^2 - \omega_C^2 x'^2) \frac{\tan[\hbar\omega_C/(2k_B T)]}{\hbar\omega_C}} \quad (\text{D3})$$

where $\omega_C = \sqrt{|V''(x_{Cc})|/m}$, $p' = p/m$, and $x' = x - x_c$. Furthermore, near the top we have from Eq. (448)

$$p' \frac{\partial W_C}{\partial x'} + \omega_C^2 x' \frac{\partial W_C}{\partial p'} = \frac{\partial}{\partial p'} \left[\gamma p' W_C + D_{p'p'} \frac{\partial W_C}{\partial p'} \right] \quad (\text{D4})$$

where $D_{p'p'} = (\gamma \hbar\omega_C/2m) \cot [\hbar\omega_C/(2k_B T)]$. Equation (D3) has the form of a Boltzmann distribution and satisfies Eq. (D4). This fact allows us to write following Kramers [15,186] the nonequilibrium solution $W(x', p')$ near the barrier as

$$W_C(x', p') = C F(x', p') e^{-\beta' (p'^2 - \omega_C^2 x'^2)} \quad (\text{D5})$$

where $C = e^{-\beta V(x_C)} \sec [\hbar\omega_C/(2k_B T)]$ and $\beta' = m \tan [\hbar\omega_C/(2k_B T)] / (\hbar\omega_C)$. The function $F(x', p')$ is a crossover function that has the equilibrium distribution in the depths of the well, varies very rapidly in the vicinity of the barrier and vanishes beyond the barrier as in the classical Kramers case [3,15]. Consequently that function must satisfy the boundary conditions

$$F(x', p') \rightarrow \begin{cases} 1, & x' \rightarrow \infty \\ 0, & x' \rightarrow -\infty \end{cases} \quad (\text{D6})$$

By substituting Eq. (D5) into Eq. (D4) and noting that $D_{p'p'} \beta' = \gamma/2$, we have the differential equation for the crossover function as in the classical case [3,15,186]

$$p' \frac{\partial F}{\partial x'} + \omega_C^2 x' \frac{\partial F}{\partial p'} = D_{p'p'} \frac{\partial^2 F}{\partial p'^2} - \gamma p' \frac{\partial F}{\partial p'} \quad (\text{D7})$$

The solution of Eq. (D7) is of the form $F(x', p') = F(p' - ax')$. By substituting $F(p' - ax')$ into Eq. (D7) and introducing a new variable $\xi = p' - ax$, we have

$$\left[(a - \gamma)p' - \omega_C^2 x' \right] \frac{\partial F}{\partial \xi} + D_{p'p'} \frac{\partial^2 F}{\partial \xi^2} = 0 \quad (\text{D8})$$

Equation (D8) simplifies to an ordinary differential equation if $\omega_C^2 = (a - \gamma)a$ or

$$a - \gamma = \sqrt{\gamma^2/4 + \omega_C^2} - \gamma/2$$

(this is the condition that the eigenvalue associated with the unstable barrier-crossing mode is real), namely,

$$(a - \gamma)\xi \frac{\partial F}{\partial \xi} + D_{p'p'} \frac{\partial^2 F}{\partial \xi^2} = 0 \quad (\text{D9})$$

The solution of Eq. (D9) satisfying the boundary conditions Eq. (D6) is

$$F(\xi) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\xi\sqrt{(a-\gamma)/2D_{p'p'}}} e^{-y^2} dy \quad (\text{D10})$$

The current j_C is then given by

$$\begin{aligned} j_c &= m \int_{-\infty}^{\infty} p' W_C(0, p') dp' \\ &= \frac{mC}{\sqrt{\pi}} \int_{-\infty}^{\infty} p' e^{-\beta' p'^2} \int_{-\infty}^{p'\sqrt{(a-\gamma)/2D_{p'p'}}} e^{-y^2} dy dp' \\ &= \frac{\hbar e^{-\beta V(x_C)}}{2 \sin [\hbar \omega_C / (2k_B T)]} \left(\sqrt{\gamma^2/4 + \omega_C^2} - \gamma/2 \right) \end{aligned} \quad (\text{D11})$$

Substituting Eqs. (D2) and (D11) into Eq. (D1) then yields the escape rate Γ^{IHD} .

APPENDIX E: JUSTIFICATION OF SEMICLASSICAL REPRESENTATION OF MATRIX ELEMENTS

The semiclassical representation of the matrix elements $\langle f | \hat{x} | j \rangle$ of the position operator \hat{x} as the Fourier transform of the classical trajectory, namely,

$$\langle f | \hat{x}(t) | j \rangle = \frac{\omega}{2\pi} \oint x_j(\tau) e^{-(i/\hbar)(E_f - E_j)(\tau - t)} d\tau \quad (\text{E1})$$

which is Eq. (370) or in Melnikov's notation (Eq. (3.8) of Ref. [8])

$$\langle \varepsilon | \hat{x}(t) | \varepsilon' \rangle = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} x(t) e^{(i/\hbar)(\varepsilon - \varepsilon')t} dt \quad (\text{E2})$$

may be briefly justified as follows. We have referring to closed librational trajectories in the well

$$E = \frac{p^2}{2m} + V(x) \quad (\text{E3})$$

$$dE = \frac{p dp}{m} = v dp \quad (\text{E4})$$

that is proceeding from infinitesimal

$$\Delta E = v \Delta p$$

or

$$\varepsilon - \varepsilon' = v(\varepsilon, x) [p(\varepsilon) - p(\varepsilon')]$$

so that

$$p(\varepsilon) - p(\varepsilon') = (\varepsilon - \varepsilon') / v(\varepsilon, x) \quad (\text{E5})$$

Hence normalizing by delta function of energy as in Ref. [23], we have

$$\langle \varepsilon | \hat{x}(t) | \varepsilon' \rangle = \int_{-\infty}^{\infty} \psi^*(\varepsilon) x \psi(\varepsilon') dx = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \frac{x dx}{v(\varepsilon, x)} e^{(i/\hbar) \int_0^x [p(\varepsilon, x') - p(\varepsilon', x')] dx'}$$

or

$$\langle \varepsilon | \hat{x}(t) | \varepsilon' \rangle = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \frac{x dx}{v(\varepsilon, x)} e^{(i(\varepsilon - \varepsilon')/\hbar) \int_0^x \frac{dx'}{v(\varepsilon, x')}} \quad (\text{E6})$$

where we have used Eq. (E5). Now since $dt = dx/v$, Eq. (E6) may be rewritten yielding Eq. (E2). For further details of semiclassical methods see [193].

REFERENCES

1. N. G. van Kampen, *Stochastic Processes in Physics and Chemistry*, North-Holland Physics Publishing, Amsterdam, 1981 3rd ed., 2007.
2. P. Hänggi, P. Talkner, and M. Borkovec, *Rev. Mod. Phys.* **62**, 251 (1990).
3. W. T. Coffey, D. A. Garanin, and D. J. McCarthy, *Adv. Chem. Phys.* **117**, 483 (2001).
4. A. Nitzan, *Chemical Dynamics in Condensed Phases*, Oxford University Press, London, 2006.
5. G. D. Billing and K. V. Mikkelsen, *Introduction to Molecular Dynamics and Chemical Kinetics*, Wiley, New York, 1996.
6. E. Pollak and P. Talkner, *Chaos* **15**, 026116 (2005).
7. V. A. Benderskii, D. E. Makarov, and C. A. Wright, *Adv. Chem. Phys.* **88**, 151–207 (1994).

8. V. I. Mel'nikov, *Phys. Rep.* **209**, 2 (1991).
9. V. I. Mel'nikov, *Physica A (Utrecht)* **130**, 606 (1985).
10. V. I. Mel'nikov and S. V. Meshkov, *J. Chem. Phys.* **85**, 1018 (1986).
11. A. I. Larkin and Yu. N. Ovchinnikov, *J. Stat. Phys.* **41**, 425 (1985).
12. E. Pollak, H. Grabert, and P. Hänggi, *J. Chem. Phys.* **91**, 4073 (1989).
13. J. S. Langer, *Ann. Phys. (N. Y.)* **54**, 258 (1969).
14. W. T. Coffey, Yu. P. Kalmykov and J. T. Waldron, *The Langevin Equation*, 2nd ed., World Scientific, Singapore, 2004.
15. H. A. Kramers, *Physica* **7**, 284 (1940).
16. H. Risken, *The Fokker–Planck Equation*, Springer, Berlin, 1984 (2nd ed., 1989).
17. C. W. Gardiner, *Handbook of Stochastic Methods*, Springer, Berlin, 1985.
18. (a) E. Pollak, *Chem. Phys. Lett.* **127**, 178 (1986); (b) E. Pollak, *J. Chem. Phys.* **85**, 865 (1986).
19. G. L. Ingold, Path integrals and their application to dissipative quantum systems, in *Coherent Evolution in Noisy Environments*, Lecture Notes in Physics, Vol. 611, Springer, Berlin, 2002, pp. 1–53
20. W. T. Coffey, Yu. P. Kalmykov, S. V. Titov, and B. P. Mulligan, *Phys. Chem. Chem. Phys.* **9**, 1 (2007); H. Lamb *Proc. London Math. Soc.* **32**, 208 (1900).
21. E. Pollak, *Phys. Rev. A* **33**, 4244 (1986).
22. U. Weiss, *Quantum Dissipative Systems*, 2nd ed., World Scientific, Singapore, 1999.
23. L. D. Landau and E. M. Lifshitz, *Quantum Mechanics: Nonrelativistic Theory*, Pergamon Press, Oxford, 1977.
24. E. Wigner, *Z. Phys. Chem. Abt. B* **19**, 203 (1932).
25. W. H. de Jeu, *Physical Properties of Liquid Crystalline Materials*, Gordon and Breach, New York, 1980.
26. W. Wernsdorfer, *Adv. Chem. Phys.* **118**, 99 (2001).
27. H. Haken, *Laser Theory*, Springer, Berlin, 1984.
28. S. Stenholm, *Foundations of Laser Spectroscopy*, Wiley, New York, 1984.
29. H. Grabert, *Phys. Rev. Lett.* **61**, 1683 (1988).
30. E. C. Titchmarsh, *An Introduction to the Theory of Fourier Integrals*, Oxford University Press, London, 1937.
31. P. M. Morse and H. Feshbach, *Methods of Theoretical Physics, Part I*, McGraw-Hill, New York, 1953.
32. H. Grabert, *Phys. Rev. Lett.* **61**, 1683 (1988).
33. H. C. Brinkman, *Physica* **22**, 29 (1956); H. C. Brinkman, *Physica* **22**, 149 (1956).
34. R. Landauer and J. A. Swanson, *Phys. Rev.* **121**, 1668 (1961).
35. R. Becker and W. Döring, *Ann. Phys. (Leipzig)* **24**, 719 (1935).
36. J. Frenkel, *The Kinetic Theory of Liquids*, Oxford University Press, London, 1946. Reprinted by Dover, New York, 1955.
37. L. J. Geoghegan, W. T. Coffey, and B. Mulligan, *Adv. Chem. Phys.* **100**, 475 (1997).
38. G. Iche and P. Nozières, *J. Phys.* **37**, 1313 (1976), G. Iche and P. Nozières, *J. Phys.* **40**, 225 (1979).
39. U. Griff, H. Grabert, P. Hänggi, and P. S. Riseborough, *Phys. Rev. B* **40**, 7295 (1989).
40. B. J. Matkowsky, Z. Schuss, and C. Tier, *J. Stat. Phys.* **35**, 443 (1984).
41. R. Zwanzig, *J. Chem. Phys.* **86**, 5801 (1987).

42. A. M. Levine, M. Shapiro, and E. Pollak, *J. Chem. Phys.* **88**, 1959 (1988).
43. A. M. Levine, W. Hontscha, and E. Pollak, *Phys. Rev. B* **40**, 2138 (1989).
44. G. Barone and A. Paterno, *Physics and Applications of the Josephson Effect*, Wiley, New York, 1982.
45. Yu. P. Kalmykov, *Phys. Rev. E* **61**, 6320 (2000); Yu. P. Kalmykov, *Phys. Rev. E* **62**, 2270 (2000).
46. M. Topaler and N. Makri, *J. Chem. Phys.* **101**, 7500 (1994).
47. A. N. Drozdov and P. Talkner, *J. Chem. Phys.* **109**, 2080 (1998).
48. H. X. Zhou, *Chem. Phys. Lett.* **164**, 285 (1989).
49. R. Ferrando, R. Spadacini, and G. E. Tommei, *Phys. Rev. A* **46**, R699 (1992).
50. R. Ferrando, R. Spadacini, and G. E. Tommei, *Phys. Rev. E* **48**, 2437 (1993).
51. R. Ferrando, R. Spadacini, G. E. Tommei, and V. I. Mel'nikov, *Phys. Rev. E* **51**, R1645 (1995).
52. W. T. Coffey, Yu. P. Kalmykov, and S. V. Titov, *J. Chem. Phys.* **124**, 024701 (2006).
53. W. T. Coffey, Yu. P. Kalmykov, S. V. Titov, and B. P. Mulligan, *Phys. Rev. E* **73**, 061101 (2006).
54. E. Pollak, J. Bader, B. J. Berne, and P. Talkner, *Phys. Rev. Lett.* **70**, 3299 (1993).
55. Yu. Georgievskii and E. Pollak, *Phys. Rev. Lett.* **70**, 5098 (1994).
56. E. Hershkovitz, P. Talkner, E. Pollak, and Yu. Georgievskii, *Surf. Sci.* **421**, 73 (1999).
57. W. T. Coffey, Yu. P. Kalmykov, and S. V. Titov, *J. Chem. Phys.* **120**, 9199 (2004).
58. Yu. P. Kalmykov, S. V. Titov, and W. T. Coffey, *J. Chem. Phys.* **123**, 094503 (2005).
59. G. J. Moro and A. Polimeno, *Chem. Phys.* **131**, 281 (1989).
60. R. W. Pastor and A. Szabo, *J. Chem. Phys.* **97**, 5098 (1992).
61. Yu. P. Kalmykov, S. V. Titov, and W. T. Coffey, *J. Chem. Phys.* **130**, 064110 (2009).
62. Yu. P. Kalmykov, S. V. Titov, and W. T. Coffey, *J. Chem. Phys.* **134**, 044530 (2011).
63. Yu. P. Kalmykov, *J. Appl. Phys.* **96**, 1138 (2004); Yu. P. Kalmykov, W. T. Coffey, B. Ouari, and S. V. Titov, *J. Magn. Magn. Mater.* **292**, 372 (2005); Yu. P. Kalmykov, W. T. Coffey, and S. V. Titov, *Fiz. Tverd. Tela (St. Petersburg)* **47**, 260 (2005) [*Phys. Solid. State* **47**, 272 (2005)]; W. T. Coffey, P. M. Déjardin, and Yu. P. Kalmykov, *Phys. Rev. B* **79**, 054401 (2009); B. Ouari, S. Aktaou, and Yu. P. Kalmykov, *Phys. Rev. B* **81**, 024412 (2010).
64. P. M. Déjardin, D. S. F. Crothers, W. T. Coffey, and D. J. McCarthy, *Phys. Rev. E* **63**, 021102 (2001).
65. J. I. Lauritzen, Jr. and R. Zwanzig, *Adv. Mol. Rel. Interact. Proc.* **5**, 339 (1973).
66. W. T. Coffey, Yu. P. Kalmykov, E. S. Massawe, and J. T. Waldron, *J. Chem. Phys.* **99**, 4011 (1993).
67. C. J. Reid, *Mol. Phys.* **49**, 331 (1983).
68. F. Marchesoni and J. K. Vij, *Z. Phys. B* **58**, 187 (1985); F. Marchesoni, *Phys. Rev. B* **32**, 1827 (1985).
69. E. Praestgaard and N. G. van Kampen, *Mol. Phys.* **43**, 33 (1981).
70. W. T. Coffey, M. W. Evans, and P. Grigolini, *Molecular Diffusion and Spectra*, Wiley, New York, 1984. Russian translation: Mir, Moscow, 1987.
71. W. T. Coffey, Yu. P. Kalmykov, and S. V. Titov, *J. Chem. Phys.* **115**, 9895 (2001).
72. M. Abramowitz and I. Stegun, eds., *Handbook of Mathematical Functions*, Dover, New York, 1964.
73. R. A. Sack, *Proc. Phys. Soc., Sect. B* **70**, 402 (1957).
74. V. I. Mel'nikov, *Phys. Rev. E* **48**, 3271 (1993); V. I. Mel'nikov, *Phys. Rev. E* **50**, 627 (1994).
75. P. Talkner and E. Pollak, *Phys. Rev. E* **47**, R21 (1993).

76. A. Szabo, *J. Chem. Phys.* **72**, 4620 (1980).
77. I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series and Products*, 4th ed., Academic Press, New York, 1980.
78. I. Rips and E. Pollak, *Phys. Rev. A* **41**, 5366 (1990).
79. C. P. Bean and J. D. Livingston, *J. Appl. Phys.* **30**, 120S (1959).
80. A. O. Caldeira and A. J. Leggett, *Physica A* **121**, 587 (1983).
81. C. Anastopoulos and J. J. Halliwell, *Phys. Rev. D* **51**, 6870 (1995).
82. R. E. Wyatt, *Quantum Dynamics with Trajectories* Springer, Berlin, 2005.
83. W. T. Coffey, D. S. F. Crothers, Yu. P. Kalmykov, and J. T. Waldron, *Phys. Rev. B* **51**, 15947 (1995).
84. D. A. Garanin, *Phys. Rev. E* **54**, 3250 (1996).
85. W. T. Coffey, D. S. F. Crothers, and S. V. Titov, *Physica A* **298**, 330 (2001).
86. J. P. Poley, *J. Appl. Sci. B* **4**, 337 (1955).
87. K. S. Gilroy and W. A. Phillips, *Philos. Mag. B* **43**, 735 (1981).
88. W. T. Coffey, D. S. F. Crothers, and Yu. P. Kalmykov, *Phys. Rev. E* **55**, 4812 (1997).
89. D. Chandler, *J. Chem. Phys.* **68**, 2959 (1978).
90. B. J. Berne, J. L. Skinner, and P. G. Wolynes, *J. Chem. Phys.* **73**, 4314 (1980).
91. D. L. Hasha, T. Eguchi, and J. Jonas, *J. Chem. Phys.* **73**, 1571 (1981); D. L. Hasha, T. Eguchi, and J. Jonas, *J. Am. Chem. Soc.* **104**, 2290 (1982).
92. D. K. Garrity and J. L. Skinner, *Chem. Phys. Lett.* **95**, 46 (1983).
93. B. Carmeli and A. Nitzan, *J. Chem. Phys.* **80**, 3596 (1984).
94. C. Blomberg, *Physica* **86A**, 49 (1977).
95. P. B. Visscher, *Phys. Rev. B* **14**, 347 (1976).
96. J. L. Skinner and P. G. Wolynes, *Chem. Phys.* **69**, 2143 (1978); J. L. Skinner and P. G. Wolynes, *J. Chem. Phys.* **72**, 4913 (1980).
97. R. S. Larson and M. D. Kostin, *J. Chem. Phys.* **69**, 4821 (1978).
98. S. C. Northrup and J. T. Hynes, *Chem. Phys.* **69**, 5246 (1978); S. C. Northrup and J. T. Hynes, *J. Chem. Phys.* **69**, 5261 (1978); S. C. Northrup and J. T. Hynes, *J. Chem. Phys.* **73**, 2700 (1980); R. F. Grote and J. T. Hynes, *J. Chem. Phys.* **73**, 2715 (1980).
99. M. Mangel, *J. Chem. Phys.* **72**, 6606 (1980).
100. K. Schulten, Z. Schulten, and A. Szabo, *J. Chem. Phys.* **74**, 4426 (1981).
101. M. Bixon and R. Zwanzig, *J. Stat. Phys.* **3**, 245 (1971).
102. M. I. Dykman, S. M. Soskin, and M. A. Krivoglaz, *Physica A* **133**, 53 (1985).
103. P. Hänggi, *Phys. Lett.* **78A**, 304 (1980).
104. J. A. Krumhansl and J. R. Schrieffer, *Phys. Rev. B* **11**, 3535 (1975).
105. J.-D. Bao and Y.-Z. Zhuo, *Phys. Rev. C* **67**, 064606 (2003).
106. V. M. Kolomietz, S. V. Radionov, and S. Shlomo, *Phys. Rev. C* **64**, 054302 (2001).
107. R. S. Larson and M. D. Kostin, *J. Chem. Phys.* **72**, 1392 (1980).
108. C. Blomberg, *Physica A* **86**, 67 (1977).
109. L. Gammaitoni, P. Hänggi, P. Jung, and F. Marchesoni, *Rev. Mod. Phys.* **70**, 223 (1998).
110. M. I. Dykman, G. P. Golubev, D. G. Luchinsky, P. V. E. McClintock, N. D. Stein, and N. G. Stocks, *Phys. Rev. E* **49**, 1935 (1994).
111. A. Schenzel and H. Brand, *Phys. Rev. A* **20**, 1628 (1979).

112. I. I. Fedchenia, *J. Phys. A: Math. Gen.* **25**, 6733 (1992).
113. Yu. P. Kalmykov, W. T. Coffey and J. T. Waldron, *J. Chem. Phys.* **105**, 2112 (1996).
114. A. Perico, R. Pratolongo, K. F. Freed, R. W. Pastor, and A. Szabo, *J. Chem. Phys.* **98**, 564 (1993).
115. B. J. Matkowsky, Z. Schuss, and E. Ben-Jacob, *J. Appl. Math.* **42**, 835 (1982).
116. C. W. Gardiner, *J. Stat. Phys.* **30**, 157 (1983).
117. Y. Onodera, *Prog. Theor. Phys.* **44**, 1477 (1970).
118. K. Voigtlaender and H. Risken, *J. Stat. Phys.* **41**, 825 (1985).
119. M. I. Dykman, R. Mannella, P. V. E. McClintock, F. Moss, and S. M. Soskin, *Phys. Rev. A* **37**, 1303 (1988).
120. J. B. Morton and S. Corrsin, *J. Stat. Phys.* **2**, 153 (1970).
121. K. Matsuo, *J. Stat. Phys.* **18**, 535 (1978).
122. K. Voigtlaender and H. Risken, *J. Stat. Phys.* **40**, 397 (1985); K. Voigtlaender and H. Risken, *Chem. Phys. Lett.* **105**, 506 (1984).
123. Yu. P. Kalmykov, W. T. Coffey, and S. V. Titov, *J. Chem. Phys.* **124**, 024107 (2006).
124. K. K. Likharev, *Dynamics of Josephson Junctions and Circuits*, Gordon and Breach, New York, 1986.
125. W. Dieterich, P. Fulde, and I. Peschel, *Adv. Phys.* **29**, 527 (1980).
126. W. W. Chow, M. O. Scully, and E. W. Van Stryland, *Opt. Commun.* **15**, 6 (1975).
127. A. J. Viterbi, *Principles of Coherent Communication*, McGraw-Hill, New York, 1966.
128. W. T. Coffey, *Adv. Chem. Phys.* **63**, 69 (1985).
129. S. G. Chung, *Phys. Rev. B* **29**, 6977 (1984).
130. W. W. Chow, J. Gea-Banacloche, L. M. Pedrotti, V. Sanders, W. Schleich, and M. O. Scully, *Rev. Mod. Phys.* **57**, 61 (1985).
131. I. Kh. Kaufman, D. G. Luchinsky, P. V. E. McClintock, S. M. Soskin, and N. D. Stein, *Phys. Rev. E* **57**, 78 (1998).
132. J. D. Cresser, D. Hammonds, W. H. Louisell, P. Meystre, and H. Risken, *Phys. Rev. A* **25**, 2226 (1982).
133. W. T. Coffey, Yu. P. Kalmykov, and E. S. Massawe, *Adv. Chem. Phys.* **85**, 667 (1993); W. T. Coffey, Yu. P. Kalmykov, and E. S. Massawe, *Phys. Rev. E* **48**, 77 (1993); W. T. Coffey, Yu. P. Kalmykov, and E. S. Massawe, *Phys. Rev. E* **48**, 699 (1993); W. T. Coffey, J. L. Déjardin, and Yu. P. Kalmykov, *Phys. Rev. E* **61**, 4599 (2000); W. T. Coffey, J. L. Déjardin, and Yu. P. Kalmykov, *Phys. Rev. B* **62**, 3480 (2000).
134. M. Büttiker, E. P. Harris, and R. Landauer, *Phys. Rev. B* **28**, 1268 (1983).
135. M. Büttiker and R. Landauer, *Phys. Rev. B* **30**, 1551 (1984).
136. Yu. P. Kalmykov, *J. Appl. Phys.* **96**, 1138 (2004).
137. J. L. García-Palacios, *Europhys. Lett.* **65**, 735 (2004).
138. J. L. García-Palacios and D. Zueco, *J. Phys. A* **37**, 10735 (2004).
139. E. Wigner, *Phys. Rev.* **40**, 749 (1932).
140. J. Ankerhold, P. Pechukas, and H. Grabert, *Phys. Rev. Lett.* **87**, 086802 (2001); J. Ankerhold, *Chaos* **15**, 0026106 (2005).
141. L. Machura, M. Kostur, P. Hänggi, P. Talkner, and J. Łuczka, *Phys. Rev. E* **70**, 031107 (2004).
142. J. Łuczka, R. Rudnicki, and P. Hänggi, *Physica A* **350**, 60 (2005).
143. D. A. Smith and F. A. de Rozario, *J. Magn. Magn. Mater.* **3**, 219 (1976).

144. W. F. Brown, Jr., *IEEE Trans. Mag.* **15**, 1196 (1979).
145. I. Klik and L. Gunther, *J. Stat. Phys.* **60**, 473 (1990).
146. W. F. Brown, Jr., *Phys. Rev.* **130**, 1677 (1963).
147. W. T. Coffey, P. J. Cregg, and Yu. P. Kalmykov, *Adv. Chem. Phys.* **83**, 263 (1993).
148. M. C. Wang and G. E. Uhlenbeck, *Rev. Mod. Phys.* **17**, 323 (1945), also reprinted in Wax cross-ref.
149. N. A. Usov, *J. Appl. Phys.* **107**, 123909 (2010).
150. P. G. Wolynes, *Phys. Rev. Lett.* **47**, 968 (1981).
151. E. Cortes, B. J. West, and K. Lindenberg, *J. Chem. Phys.* **82**, 2708 (1985).
152. A. O. Caldeira and A. J. Leggett, *Ann. Phys.* **149**, 374 (1983).
153. E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations*, McGraw-Hill, 1955.
154. P. Pechukas, in *Dynamics of Molecular Collisions*, part B, W. H. Miller, ed., Plenum Press, New York, 1976, Chapter 6.
155. P. Hänggi and G. L. Ingold, *Chaos* **15**, 026105 (2005).
156. D. Kohen and D. J. Tannor, *Adv. Chem. Phys.* **111**, 219 (1994).
157. M. Hillery, R. F. O'Connell, M. O. Scully, and E. P. Wigner, *Phys. Rep.* **106**, 121 (1984); V. I. Tatarskii, *Uspekhi Fiz. Nauk* **139**, 587 (1983) [*Sov. Phys. Uspekhi* **26**, 311 (1983)].
158. H. W. Lee, *Phys. Rep.* **259**, 147 (1995).
159. W. P. Schleich, *Quantum Optics in Phase Space*, Wiley-VCH, Weinheim, 2001.
160. R. Kapral, *Annu. Rev. Phys. Chem.* **57**, 129 (2006).
161. N. Makri, *J. Math. Phys.* **36**, 2430 (1995).
162. C. H. Mac and R. Egger, *Adv. Chem. Phys.* **93**, 39 (1995).
163. A. G. Redfield, *IBM J. Res. Dev.* **1**, 19 (1957).
164. Y. J. Yan, F. Shuang, R. Xu, J. Cheng, X. Q. Li, C. Yang, and H. Zhang, *J. Chem. Phys.* **113**, 2068 (2000).
165. H. Grabert, P. Schramm, and G. L. Ingold, *Phys. Rep.* **168**, 115 (1988).
166. H. T. Davis, K. Hiroike, and S. A. Rice, *J. Chem. Phys.* **43**, 2633 (1965).
167. Y. Tanimura and P. G. Wolynes, *J. Chem. Phys.* **86**, 8485 (1992).
168. S. Zhang and E. Pollak, *J. Chem. Phys.* **118**, 4357 (2003).
169. G. S. Agarwal, *Phys. Rev. A* **4**, 739 (1971).
170. H. Dekker, *Phys. Rev. A* **16**, 2116 (1977).
171. J. J. Halliwell and T. Yu, *Phys. Rev. D* **53**, 2012 (1996).
172. R. Karrlein and H. Grabert, *Phys. Rev. E* **55**, 153 (1997).
173. G. W. Ford and R. F. O'Connell, *Phys. Rev. D* **64**, 105020 (2001).
174. W. T. Coffey, Yu. P. Kalmykov, S. V. Titov, and B. P. Mulligan, *Europhys. Lett.* **77**, 20011 (2007).
175. W. T. Coffey, Yu. P. Kalmykov, S. V. Titov, and B. P. Mulligan, *J. Phys. A: Math. Theor.* **40**, F91 (2007).
176. Yu. P. Kalmykov, W. T. Coffey, and S. V. Titov, *Physica A*, **377**, 412 (2007).
177. D. Barik, B. C. Bag, and D. S. Ray, *J. Chem. Phys.* **119**, 12973 (2003).
178. R. Kubo, *J. Phys. Soc. Jpn.* **12**, 570 (1957); R. Kubo, M. Toda, and N. Hashtsume, *Statistical Physics II. Nonequilibrium Statistical Mechanics*, 2nd ed., Springer, Berlin, 1991.
179. S. R. de Groot and L. G. Suttorp, *Foundations of Electrodynamics*, North-Holland, Amsterdam, 1972, Chapters VI and VII.
180. J. T. Stockburger and C. H. Mak, *J. Chem. Phys.* **110**, 4983 (1999).

181. R. Ferrando, R. Spadacini, and G. E. Tommei, *Nuovo Cim. D* **15**, 557 (1993).
182. S. Miret-Artés and E. Pollak, *J. Phys.: Condens. Matter* **17**, S4133 (2005).
183. Yu. Georgievskii and E. Pollak, *Phys. Rev. E* **49**, 5098 (1994).
184. Y. Tanimura and P. G. Wolynes, *Phys. Rev. A* **43**, 4131 (1991).
185. V. I. Mel'nikov and A. Sütö, *Phys. Rev. B* **34**, 1514 (1986).
186. P. Hänggi, H. Grabert, G. L. Ingold, and U. Weiss, *Phys. Rev. Lett.* **55**, 761 (1985).
187. R. L. Stratonovich, *Topics in the theory of Random Noise*, Vol. 1, Gordon and Breach, New York (1963).
188. Yu. P. Kalmykov, *Khim. Fiz.* **6**, 745 (1987) [Sov. J. Chem. Phys. **6**, 1427 (1990)].
189. E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis*, 4th ed., Cambridge University Press, Cambridge, 1927.
190. H. T. Davis, *Introduction to Nonlinear Differential and Integral Equations*, Dover, New York, 1962.
191. A. Prudnikov, Yu. A. Brychkov, and O. I. Marichev, *Integrals and Series, More Special Functions*, Vol. 3, Gordon and Breach, New York, 1990.
192. S. V. Titov, P. M. Déjardin, and Yu. P. Kalmykov, *J. Chem. Phys.* **120**, 4852 (2004).
193. D. S. F. Crothers, *Semiclassical Dynamics and Relaxation*, Springer Verlag, Berlin, (2008).